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PREPARATION AND CHARACTERIZATION OF CATALYSTS FOR PROTON EXCHANGE MEMBRANE FUEL CELL

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ABSTRACT (ENGLISH)

Nowadays, the growing demand of energy, the depletion of fossil fuels and the negative consequences of their use make necessary the development of a new technology able to mitigate the situation. Hydrogen technology can be a solution because hydrogen can generate electricity directly from its chemical energy. PEM fuel cells are the main convertor system. This master thesis focuses on the improvement of the catalyst cathode from fuel cells that is an essential component of fuel cells. One of the most often catalyst used is the Platinum, an expensive noble metal. It makes the development of fuel cell technologies expensive and as consequence, fuel cells are not commercialised globally. In order to optimise the use of Platinum and improve the efficiency of fuel cells, it has been studied the power density obtained from several catalysts. Every catalyst has been prepared with different ratios of Nafion/carbon, Teflon/carbon, amounts of Platinum (mg/cm^2) and also it has been varied the type of catalyst powder used (Pt/C 30%, Pt/C 40% y Pt/C 50%). In addition, the influence of annealing the samples after the spraying has been studied in contrast to samples not annealed. Moreover, the power density used as reference from commercial catalyst to know the quality of catalysts prepared is $1 \text{ W}/\text{cm}^2$ for a hydrogen-oxygen fuel cell, and $0.5 \text{ W}/\text{cm}^2$ hydrogen-air fuel cell. The surface of catalysts has been analysed by Scanning Electron Microscopy (SEM) with the purpose to understand better the behaviour of these. Finally, it has been selected one of the catalyst that has showed better power density to be tested into a stack of single fuel cells under standard conditions of temperature and pressure and without humidify system.

Keywords: PEM fuel cells, cathode, catalyst, Platinum, Nafion, Teflon, power density, Scanning Electron Microscopy.

RESUMEN (SPANISH)

En la actualidad, la creciente demanda de energía, el agotamiento de los combustibles fósiles y las consecuencias negativas de su uso hacen necesario el desarrollo de nuevas tecnologías que palién la situación de un modo global, eficiente y limpio. La tecnología del hidrógeno puede ser una solución: obtener electricidad directamente a partir de la energía química que almacena esta sustancia, cuyo sistema de conversión principal son las celdas de combustible tipo PEM. Este trabajo se centra en la mejora del catalizador del cátodo de las celdas de combustible. Este componente de la celda es indispensable para su funcionamiento y uno de los mejores catalizadores de los que se dispone es el Platino, una metal noble y caro que hace que el desarrollo de esta tecnología sea muy caro y como consecuencia no se comercialice globalmente. Para optimizar el uso del Platino y mejorar la eficiencia de la celda de combustible se ha estudiado la densidad de potencia obtenida a partir de diferentes catalizadores. Cada catalizador ha sido preparado con diferentes ratios de Nafion/Carbono, Teflón/Carbono, diferentes contenidos de Platino en miligramos por centímetro cuadrado y también se ha variado el tipo de polvo de Platino en Carbono utilizado (Pt/C 30%, Pt/C 40% y Pt/C 50%). Además, se ha estudiado la influencia de calentar las muestras de catalizador después de su preparación y antes de ser testadas en la estación de testado de celdas de combustible con respecto a muestras con el mismo catalizador, pero sin ser sometidas a calor. Con todos estos resultados se pretende alcanzar un catalizador que maximice la potencia de la celda de combustible trabajando a las mismas condiciones de temperatura, presión y humedad. Asimismo, para conocer la calidad de los catalizadores obtenidos se ha tomado como referencia un catalizador comercial que alcanza una potencia de 1 vatio por centímetro cuadrado de catalizador para flujos de gas de alimentación hidrógeno-oxígeno, y 0,5 W/cm² de potencia para un flujo de gases hidrógeno-aire. La superficie de los catalizadores ha sido estudiada mediante microscopio electrónico de barrido (SEM) para entender mejor el comportamiento de estos. Finalmente, ha sido seleccionado uno de los catalizadores que han mostrado mejores resultados para ser testado en una stack de monoceldas de pilas de combustible en condiciones de normales de temperatura y presión y sin sistema de humidificación.

Palabras clave: celdas de combustible tipo PEM, cátodo, catalizador, Platino, Nafion, Teflón, densidad de potencia, microscopio electrónico de barrido, stack de monoceldas.

RESUM (CATALAN)

A l'actualitat, la creixent demanda d'energia, l'esgotament de combustibles fòssils i les conseqüències negatives relatives a la seua utilització fan necessari el desenvolupament de noves tecnologies que pal·lien la situació de un mode global, eficient i net. La tecnologia de l'hidrogen pot resultar una solució: obtenir electricitat directament a partir de l'energia química continguda en aquesta substància, sistema principal de conversió de la qual són les cel·les de combustible tipus PEM. Aquest treball se centra en la millora del catalitzador del càtode de les cel·les de combustible. Aquest component de la pila es indispensable per al seu funcionament i un del millors catalitzadors de que es disposa es el Platí, un metall noble i car que fa que el desenvolupament d'aquesta tecnologia sigui cara i com a conseqüència no es comercialitzi globalment. Per optimitzar l'ús del Platí i millorar l'eficiència de la cel·la de combustible s'ha estudiat la densitat de potència obtinguda a partir de diferents catalitzadors. Cada catalitzador ha esta preparat amb diferents ràtios de Nafion/carboni, tefló/carboni, diferents continguts de platí (mg/cm^2 de catalitzador) i també s'ha variat el tipus de pols de platí en carboni utilitzat (Pt/C 30%, Pt/C 40% y Pt/C 50%). A més, s'ha estudiat la influencia d'escalfar les mostres de catalitzador després de la seua preparació i abans de ser testades a la estació de testat de cel·les de combustible respecte de la mostra amb el mateix catalitzador sense haver estat sotmès a calor. Amb tots aquests resultats, es pretén obtindre un catalitzador que maximitzi la potència de la pila de combustible treballant a les mateixes condicions de temperatura, pressió i humitat. Amb tot això, per conèixer la qualitat dels catalitzadors obtinguts es pren com a referència un catalitzador comercial que aconsegueix una potència de $1 \text{ W}/\text{cm}^2$ de catalitzador de potència per a un flux de gasos d'alimentació d'hidrogen-oxigen pur i $0,5 \text{ W}/\text{cm}^2$ de potència per a un flux de gasos hidrogen-aire. La superfície dels catalitzadors ha estat estudiada mitjançant un microscopi electrònic de rastreig (SEM) per entendre millor el comportament d'aquests. Finalment, ha sigut seleccionat un del catalitzadors que ha mostrat millors resultats per a ser testat a una stack de monocel·les de combustible en condicions normals de temperatura i pressió i sense sistema de humidificació.

Paraules clau: cel·la de combustible tipus PEM, càtode, catalitzador, Platí, Nafion, tefló, densitat de potència, microscopi electrònic de rastreig, stack de monocel·les.

CONTENTS

ACKNOWLEDGEMENT	2
ABSTRACT (ENGLISH).....	4
RESUMEN (SPANISH)	6
RESUM (CATALAN).....	8
CONTENTS.....	10
1. THE GOALS OF THE MASTER THESIS	12
2. INTRODUCTION.....	13
2.1. GLOBAL ENERGY CONTEXT	13
2.2. HYDROGEN ECONOMY	18
2.3. FUEL CELLS	20
2.3.1. Brief history of fuel cell origins.....	20
2.3.2. Fuel cell principles	21
2.3.3. Types of Fuel Cells.....	22
2.3.4. Fuel Cell advantages.....	25
2.3.5. Main applications of Fuel Cells.....	25
2.4. PROTON EXCHANGE MEMBRANE FUEL CELL (PEM FC).....	26
2.4.1. PEM FC principle.....	26
2.4.2. Elements of a PEM Fuel Cell	27
2.4.3. Fuel Cell Performance.....	31
2.4.4. Fuel cell stack	32
3. EXPERIMENTAL DESIGN	32
3.1. INK FORMULATION	33
3.2. INK DEPOSITION	35
3.2.1. GDL preparation.....	35
3.2.2. Sonicated spraying.....	35
3.2.3. Heating of the samples	36

3.3.	FUEL CELL CHARACTERIZATION TECHNIQUES	36
3.3.1.	Fuel Cell Assembly	36
3.3.2.	Fuel Cell Testing.....	37
4.	EXPERIMENTAL RESULTS AND DISCUSSION.....	39
4.1.	EFFECT OF SPRAYING NOZZLE HEIGHT	39
4.2.	DIFFERENCES BETWEEN n-GDL AND GDL.....	40
4.3.	EFFECT OF THE CARBON POROSITY.....	41
4.4.	EFFECT OF THE TEFLON CONTENT	42
4.5.	EFFECT OF THE NAFION CONTENT.....	43
4.6.	INFLUENCE OF THE TYPE OF CATALYST POWDER.....	44
4.7.	DIFFERENCES BETWEEN ANNEALED AND NOT ANNEALED SAMPLES	46
4.8.	INFLUENCE OF PLATINUM LOADING	47
5.	CONCLUSIONS.....	52
6.	BIBLIOGRAFY	53

1. THE GOALS OF THE MASTER THESIS

Present master thesis is focused on the preparation and characterization of cathode catalysts for Proton Exchange Membrane Fuel Cell composed of Platinum on Carbon. Platinum is the most suitable material allowing to get a good power density for real PEM FC application but also it is a very expensive material. Therefore, the aim of this work is to find a cathode catalyst able to produce a high power density with the minimum content of Platinum.

With the purpose to achieve the main target of this thesis, catalysts are prepared varying their composition. Every sample is prepared using spraying method and its power density is known by experimental test in fuel cell test station. Moreover, the morphology of superficial layer can be observed by Scanning Electron Microscopy (SEM) that helps to understand the possible behaviour of samples.

Main individual goals of this work are listed below:

- Prepare Pt/C catalyst cathode using spraying method.
- Direct test of catalyst cathode in PEM FC test station with commercial catalyst anode using a flow of pure hydrogen and a flow of pure oxygen, followed by a flow of pure hydrogen and normal air.
- Analyse the power density obtained from samples with the same composition but different Pt loading.
- Study how the content of Nafion in cathode catalyst has influence in the power density of the fuel cell.
- Study the effects of using different ratios of Teflon/Carbon in the cathode catalyst performance.
- Investigate the final behaviour of catalysts using different commercial powders with a different percentage of Platinum on Carbon (Pt/C 30%, Pt/C 40%, Pt/C 60%) in the ink preparation.
- Discover the influence of heating samples after spraying on the power density in comparison with the same sample (same ink catalyst) not annealed.
- Compare results with commercial Pt catalyst.

2. INTRODUCTION

2.1. GLOBAL ENERGY CONTEXT

The growth and development of humanity are closely linked to the consumption of natural resources and energy. Throughout history world population has grown slowly but in recent centuries, the number of inhabitants has increased from 1 billion in the nineteenth century to 7 billion in October 2011 (United Nations, 2011). Figure 2.1 shows the estimate of world population growth from 10,000 BC to AD 2000. This population increment coincides with the First and Second Industrial Revolutions, which had taken place since the late eighteenth century. From that moment, the traditional economy based on agriculture started a transition towards an economy more industrialized and mechanized. As result, the demand for raw materials and new energy sources increased. Specifically, over the First Industrial Revolution and because of the invention of steam engine, coal began to be more widely used. At the end of the nineteenth century, with the beginning of the Second Industrial Revolution and due to the invent of the internal combustion engine, the oil consumption shoots up to detriment of coal. Figure 2.2 shows the annual power consumption of the United States since 1775. Industrialization arrived later than countries as United Kingdom, however, it can be seen the tendency of coal and oil consumption described above.

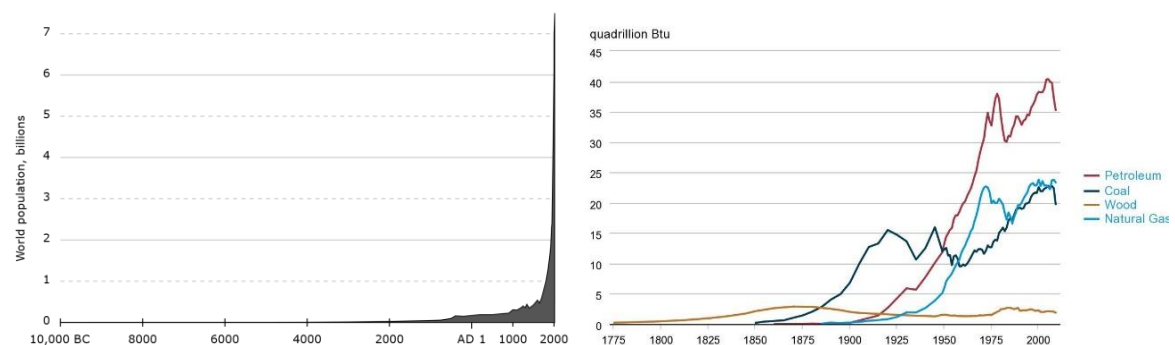


Figure 2.1. Estimated world population from 10,000 BC to AD 2000.

Figure 2.2. History of energy consumption in the United States, 1775-2009. Source: “Annual Energy Review 2009” by U.S. Energy Information Administration. Retrieved May 2018.
<https://www.eia.gov/todayinenergy/detail.php?id=10#>

Nowadays, power consumption has increased dramatically due to, principally, the arrival of the Digital Era and continued development of countries. In addition, present world population has reached 7.3 billion people and it is estimated that the population will reach 11 billion by the end of this century. It can be seen in Figure 2.3 the different projections about the population growth done by the United Nation in 2017. Energy model that holds this rate of growth is based on fossil fuel consumption such as oil, coal and gas. Specifically, around 85.5% of global energy consumption was produced by fossil in 2016 as can be seen in Figure 2.4. Among them, crude oil was the most commonly consumed and it remains the world's dominant fuel with almost 33.5% of global primary energy consumption.

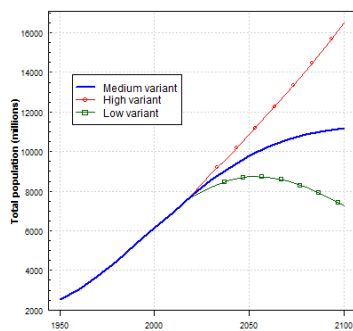


Figure 2.3. Total population by variant for dates between 1950-2100. Source: “World Population Prospects 2017” by United Nations. Retrieved May 2018. <https://esa.un.org/unpd/wpp/Graps/DemographicProfiles/>.

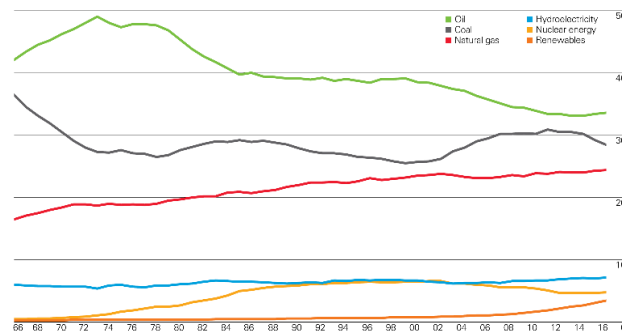


Figure 2.4. Shares of global primary energy consumption (percentage) from 1966 to 2016. Source: “Statistical Review of World Energy 2017” by BP. Retrieved May 2018. <https://www.bp.com/content/dam/bp/en/corporate/pdf/energy-economics/statistical-review-2017/bp-statistical-review-of-world-energy-2017-full-report.pdf>.

Nevertheless, the use of fossil fuels has several political, economic and ecological impacts. Historically, geopolitical conflicts have taken place to have control of the exploitation of oil and gas reserves. These conflicts contribute to rise and volatility of prices. For example, there was a sharp rise in oil prices owing to the 1973 Oil Crisis and, more recently, the price per barrel escalated to more than USD 100 after the Invasion of Iraq and, once again, after demonstrations during Arab Spring (see Figure 2.5).

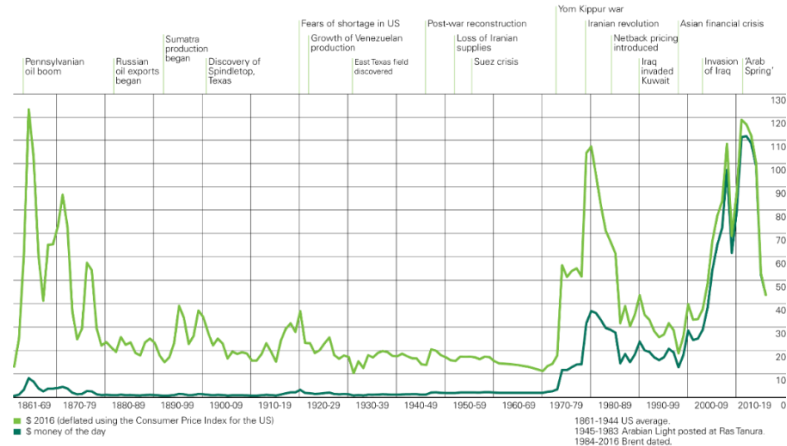


Figure 2.5. Crude oil price 1861-2016. US dollars per barrel, world events. Source: “Statistical Review Energy 2017” by BP. Retrieved May 2018.

<https://www.bp.com/content/dam/bp/en/corporate/pdf/energy-economics/statistical-review-2017/bp-statistical-review-of-world-energy-2017-full-report.pdf>

Furthermore, combustion of fossil fuels emits gasses and other toxic pollutants, mainly carbon dioxide (CO_2) and methane (CH_4), that contribute to the greenhouse effect. Figure 2.6 illustrates the world energy-related CO_2 emissions from 1966 to 2016. It is seen that carbon emissions increased by 55% in the past 25 years and much of the growth is attributed to the developing of nations from Asia. Last years, after no growth from 2014 to 2016, emissions grew by 1.6% to 33.4 billion metric tons. Projections say that CO_2 emissions will rise to 39.3 billion metric tons in 2040 because of the use of liquid fuels and gas natural mostly, while coal-related CO_2 emissions will remain constant as Figure 2.7 shows.



Figure 2.6. Carbon dioxide emissions (million tons of equivalent) from 1966 to 2016. Source: by BP energy charting tool. Retrieved May 2018.
<https://www.bp.com/en/global/corporate/energy-economics/energy-charting-tool-desktop.html>.

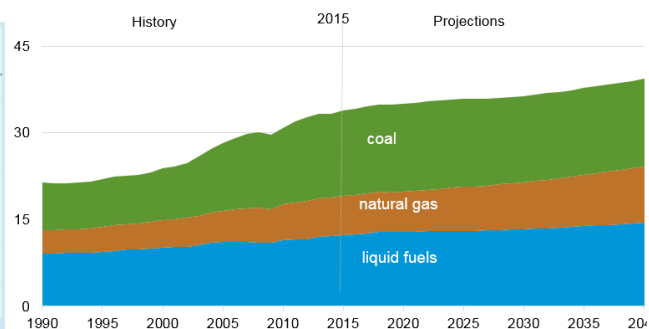


Figure 2.7. Projections world energy-related dioxide emissions (billion metric tons) by fuel type. Source: “International energy summary 2017” by U.S. Energy Information Administration. Retrieved May 2018.
https://www.eia.gov/outlooks/ieo/pdf/exec_summary.pdf.

Concentration of carbon dioxide in the atmosphere is directly related to the global warming. The CO₂ atmospheric level has climbed drastically over the past 70 years. The latest analysis of observations from the WMO GAW Programme shows that, over the last 800 000 years, atmospheric CO₂ content remained below 280 parts per million, but it has risen to 403.3 ppm in 2016 (see the Figure 2.8 below). Concentrations of CO₂ are now 145% of pre-industrial levels.

It is difficult to predict the consequences of the warming, but some environmental changes can be detected: acidifying oceans, more extreme weather, glacier melting and sea-level rise (Kump, 2011). In order to combat climate change, 195 nations signed the Paris Agreement during the 21st Conference of Parties (COP21). Paris agreement took place under the United Nations Framework Convention on Climate Change (UNFCCC), as Kyoto Protocol was previously on 1997. The aim of the agreement is described in its Article 2: “Holding the increase in the global average temperature to well below 2 °C above pre-industrial levels” (FCCC, 2015).

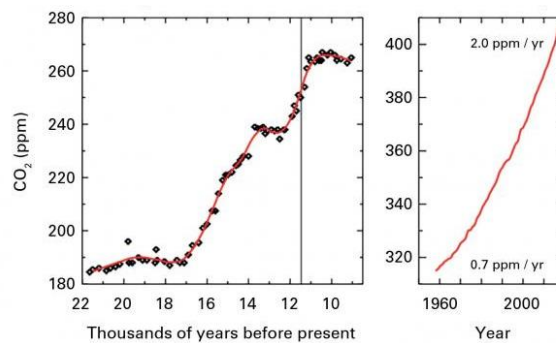


Figure 2.8. CO₂ atmospheric content at the end of the last ice age (left) and recent CO₂ atmospheric content (right). Source: “Greenhouse gas bulletin 2017” by World Meteorological Organization.

Retrieved May 2018. https://ane4bf-datap1.s3-eu-west-1.amazonaws.com/wmocms/s3fs-public/ckeditor/files/GHG_Bulletin_13_EN_final_1_1.pdf?LGJNmHpwKkEG2Qw4mEQjdm6bWxgWAJHa

But, despite the unfavourable data and the established connections between the fossil fuels consumption and the CO₂ atmospheric content, the fact remains that the world energy consumption will continue rising annually. Figure 2.9 shows an average growth of 1.8% last 10 years and consumption peaked in 2016 at 13 276.31 million tonnes oil equivalent (mtoe). Moreover, it is expected that the total world consumption grew by 28% from 2015 to 2040 (U.S. Energy Information Administration, 2017), especially in countries from Asia Pacific due to a strong economic growth and a quickly growing population.

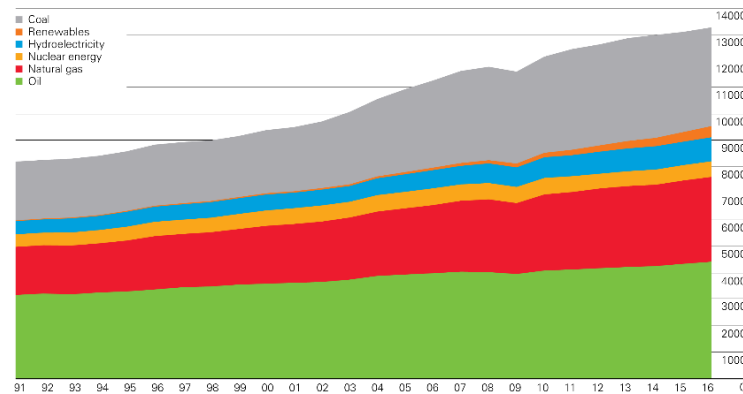


Figure 2.9. Primary energy world consumption (million tonnes oil equivalent). Source: “BP Statistical Review of World Energy 2017” by BP. Retrieved May 2018. <https://www.bp.com/content/dam/bp/en/corporate/pdf/energy-economics/statistical-review-2017/bp-statistical-review-of-world-energy-2017-full-report.pdf>

With reference to the location of current fossil fuel reserves, most of them are owned by countries from Middle East. In 2017, it was proved that the global oil stock is 1.7 billion barrels. By region, Middle East holds the half of the reserves followed by South and Central America (19.5%), see Figure 2.10. Based on data from BP, proved gas reserves are 193.5 trillion cubic meters (tcm) in 2017. The Middle East is the largest contributor to reserves (40.9%) and CIS region also adds 30.6% of the global total. These fuel reserves are sufficient to meet around 50 years of global production at 2017 levels. Nevertheless, the available reserve projections of fossil fuels could vary with the growth rate of energy consumption.

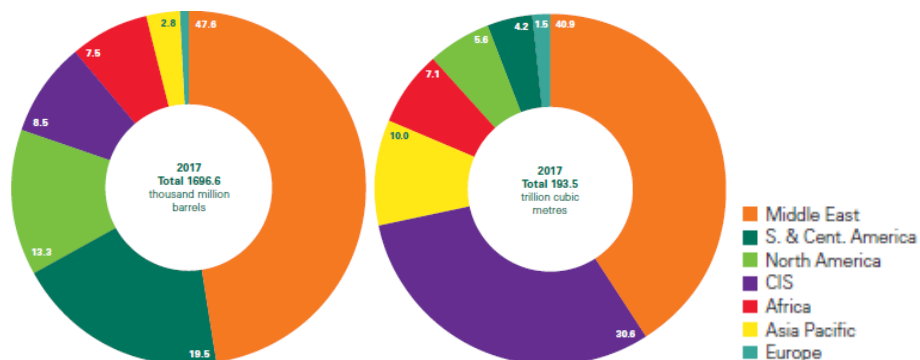


Figure 2.10. Distribution of proved reserves in 2017. Thousand million barrels of oil (left) and billion cubic metres of gas (right) Source: “BP Statistical Review of World Energy 2017” by BP. Retrieved May 2018. <https://www.bp.com/content/dam/bp/en/corporate/pdf/energy-economics/statistical-review-2017/bp-statistical-review-of-world-energy-2017-full-report.pdf>

In face of exhaustion of fossil fuels, the difficult of knowing exactly the amount of fuel reserves and due to the environmental damage caused by their use, for decades it has been

discussed about the need to develop an energy system that keeps growth of nations, improve the standard of livings of the whole population and eliminate the world reliance on fossil fuels. In this context, hydrogen technology is a clean and renewable option for achieving these goals.

2.2. HYDROGEN ECONOMY

Hydrogen is the most abundant element in the universe. It is a colourless and odourless gas that account for 75% of the universe mass (Momirlan, 2005). An atom of hydrogen consists of one proton and one electron, but, despites its simplicity, hydrogen can be found on Earth only in combination with other elements. Water and hydrocarbons are compounds formed by hydrogen plus oxygen and hydrogen plus carbon, respectively. Consequently, hydrogen must be separated from these other elements in order be used as fuel. This imply that hydrogen is not a primary energy resource, but an energy vector.

An energy vector is a tool allows to transfer and storage energy (Orecchini, 2006), also named secondary energy source. So, hydrogen economy is based on the use of hydrogen as energy vector for produce electricity and heat. Nonetheless, it cannot be said that the energetic crisis will be solved only with hydrogen.

A complex energy system is constituted by different parts: primary energy sources, technologies for transport, storage, conversion and final uses of energy, interaction with the environment and waste production (Orecchini, 2006). In one of the most interesting scenarios, energetic system is based on hydrogen economy and hydrogen is obtained by electrolysis from water and produced by a renewable primary resource, it is transported to the end use point where is stored until there is an energy demand, see Figure 2.11.

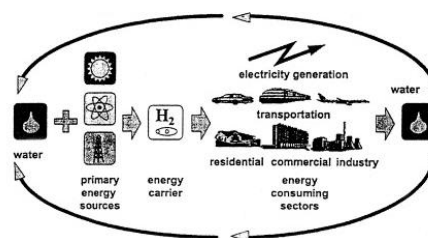


Figure 2.11. Hydrogen Economy. Source: “Current status of hydrogen energy” by Mormirlan, M., 2002, Renewable & Sustainable energy reviews, p.163.

There are four main advantages of that system. First of all, there is not risk of limited resources because water is abundant on Earth. In addition, the water consumed to produce hydrogen reappears as by-product during the hydrogen reduction reaction.

In second place, the use of hydrogen in fuel cells has from very low to zero carbon emissions and no emissions of damaging air substances such as nitrogen dioxide, sulphur dioxide or carbon monoxide (High level group on Hydrogen and Fuel Cells, 2003), in case hydrogen was produced by a renewable energy source (e.g. wind, solar, ocean, and biomass).

Thirdly, hydrogen enables to store renewable energy in time, so that the demand of energy can be satisfied continuously despite the intermittent nature of renewable energy sources and the supply is adapted to regional circumstances. In brief, supply can be adjusted to demand, see Figure 2.12 left.

Finally, hydrogen can also transfer renewable energy in space enabling to fit the place where the energy is generated to the place of use. This characteristic is interesting for applications like portable power, emergency back-up power and auxiliary power units in which primary energy cannot be used, see Figure 2.12 right.

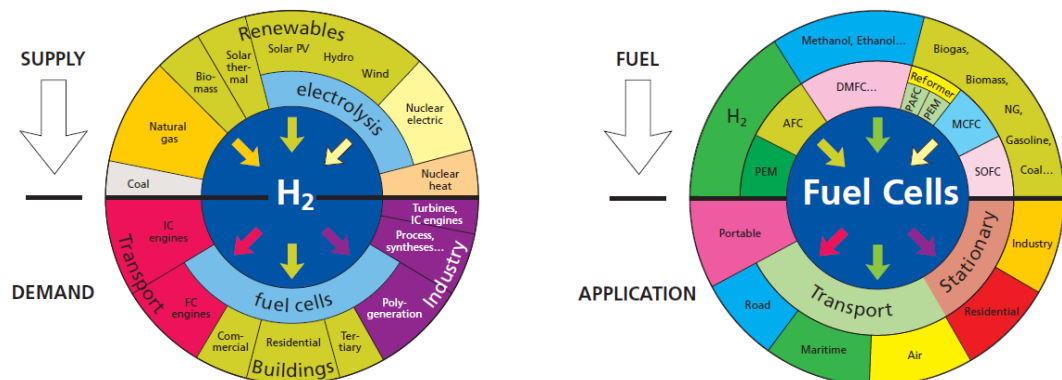


Figure 2.12. Fuel cell technologies, possible fuels and applications (left). Hydrogen: primary energy sources, energy converters and applications (Right). Source: “Hydrogen Energy and Fuel Cells. A vision of our future.” by High Level Group. 2003. p. 11,12.

http://www.fch.europa.eu/sites/default/files/documents/hlg_vision_report_en.pdf

The actual challenge of the hydrogen economy consists of the development of a system able to generate hydrogen from non-polluting sources, make progress in enhancing the hydrogen storage procedure, design a conversion system that transform hydrogen into electricity efficiently and establish a hydrogen infrastructure through global partnerships to cause the revolution toward a global hydrogen use (Momirlan, 2005). Besides these

difficulties, the costs of the technology are high, it is not produced on a large scale because there is not demand and there is not demand due to the high cost. This is therefore the chicken and egg question. In this way, hydrogen is not penetrating on the market completely. However these facts, hydrogen is a sustainable fuel and the solution to the depletion of conventional fuels and global environmental problems.

But, how can hydrogen be used as fuel? It is possible to obtain useful work by burning hydrogen in an internal combustion engines (ICE). Briefly, it is a heat engine that uses hydrogen as fuel and it works as a traditional gasoline-powered internal combustion engine (US Department of energy, 2001). ICE cycle includes an intermediary heat phase, restricting potential efficiency to ideal heat limits (Pearson, Leary, & Subic, 2011). On average, hydrogen ICE can achieve a 40% of efficiency. But, nowadays, electricity is one of the growing forms of end use of energy so that, it would be necessary to use an electric generator that would make the hydrogen ICE efficiency even lower.

On the other hand, it is available a power unit that can convert the chemical energy contained in hydrogen to electrical energy directly. It is called fuel cell (FC). In comparison, the efficiency of FC can achieve an efficiency of 55% on average and it can increase up to 65% (Gillingham, 2007). This direct form of obtained electricity is what makes the study and develop of fuel cells interesting.

2.3. FUEL CELLS

2.3.1. Brief history of fuel cell origins

The development of fuel cells dates from the nineteenth century, before even the invention of the electric motor, the steam turbine of the internal combustion engine. It was in 1839 when the barrister Willian Grove invented the first fuel cell based on a couple of platinum electrodes immersed in very dilute sulfuric acid (Blomen & Mugerwa, 1993), Figure 2.13 shows four cells of a battery built by Grove (Hoogers, 2003). During one century, scientists and engineers like William Grove, William W. Jacques, Ludwig Mond, Carl Haber and Walther Nernst worked on different types of fuel cells, precursors of the present fuel cells but, after 1940 fuel cell progress decreased his intensity. In 1961, Francis Bacon developed the first real application for fuel cells: a battery for the Apollo space mission. The battery consisted of three units of 100 kg each with 31 cells in series. Each unit could deliver a

maximum of 2.295 kW at a minimum voltage of 20.5V. Due to the high weight, the commercialization for other applications was complicated.

Last century, due to the different fuel crisis, governments started to be interested in investing in new technologies for transport and stationary power production and many projects were financed.

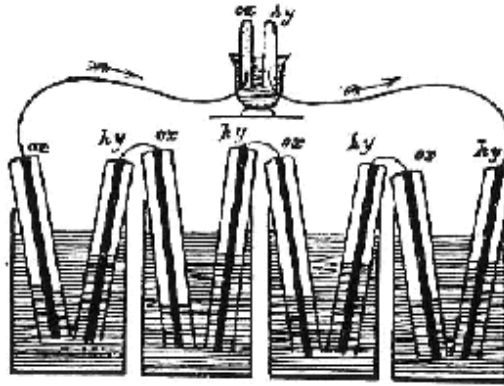


Figure 2.13. Gas battery built by Grove (1942).

2.3.2. Fuel cell principles

Fuel Cell is an electrochemical device able to transform chemical energy stored in a fuel into electrical energy. The fuel cell consists of two electrodes (anode and cathode) and an electrolyte, following a scheme as shown Figure 2.14. Consider a fuel cell that works with hydrogen. Hydrogen is oxidized within the anode and this produces protons and electrons, see equation (1). The protons can flow through the electrolyte to the cathode side, but the electrons cannot. Electrons move across the outer circuit and reach the cathode side. They recombine with protons and react with the oxidant (i.e. oxygen, see equation (2)) within the cathode and produce water and heat.



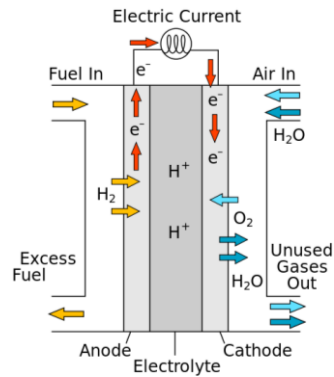


Figure 2.14. Scheme of a proton-conduction fuel cell. Source: Wikipedia. Public domain. https://en.wikipedia.org/wiki/Fuel_cell#/media/File:Solid_oxide_fuel_cell_protonic.svg

2.3.3. Types of Fuel Cells

There are five main types of fuel cells and all of them are differentiated due to their electrolyte. These fuel cell types are phosphoric acid fuel cell (PAFC), proton exchange membrane fuel cell (PEMFC), alkaline fuel cell (AFC), molten carbonate fuel cell (MCFC), and solid oxide fuel cell (SOFC). They will be briefly introduced in the following section. Main characteristics are described in Table 2.1.

Table 2.1. Description of major fuel cell types. Source: “Fuel cell fundamentals” by O’Hayre R. 2016. <https://onlinelibrary.wiley.com/doi/pdf/10.1002/9781119191766>

	PEMFC	PAFC	AFC	MCFC	SOFC
Electrolyte	Polymer membrane	Liquid H ₃ PO ₄ (immobilized)	Liquid KOH (immobilized)	Molten carbonate	Ceramic
Charge carrier	H ⁺	H ⁺	OH ⁻	CO ₃ ²⁻	O ²⁻
Operating temperature	80°C	200°C	60–220°C	650°C	600–1000°C
Catalyst	Platinum	Platinum	Platinum	Nickel	Perovskites (ceramic)
Cell components	Carbon based	Carbon based	Carbon based	Stainless based	Ceramic based
Fuel compatibility	H ₂ , methanol	H ₂	H ₂	H ₂ , CH ₄	H ₂ , CH ₄ , CO

2.3.3.1. Phosphoric acid fuel

In PAFC, electrolyte is liquid H₃PO₄. It is contained in a thin SiC matrix between two graphite electrodes coated with platinum catalyst (O’Hayre & Suk-Won, 2016). The fuel is hydrogen that is oxidized by oxygen from air. The anode and cathode reactions are:



The SiC matrix provides mechanical strength to the electrolyte, keeps the two electrodes separated, and minimizes reactant gas crossover. During operation, H_3PO_4 must be continually replenished because it gradually evaporates to the environment. Electrical efficiencies of PAFC units are 40%. One of the disadvantages is the use of platinum as catalyst because of the high cost.

2.3.3.2. Proton exchange membrane fuel cell

This type of fuel cell is widely commented on paragraph 2.4 because PEMFC is the object of study of the present master thesis.

2.3.3.3. Alkaline fuel cell

The AFC employs an aqueous potassium hydroxide electrolyte and OH^- are conducted from the cathode side to the anode side. The reactions that taking place are:



The water is consumed at the cathode and it is produced faster at anode. The water must be removed to prevent the dilution of the KOH electrolyte. Because of many more metal-based catalysts are stable in an alkaline environment, nickel (rather than platinum) catalyst can be used as the cathode catalyst. This type of fuel cell needs pure flow of fuel gases because the presence of CO_2 can degrade the KHO electrolyte.

2.3.3.4. Molten carbonate fuel cell

The electrolyte in the MCFC is a molten mixture of alkali carbonates, Li_2CO_3 and K_2CO_3 , immobilized in a $LiO-AlO_2$ matrix (O'Hayre & Suk-Won, 2016). CO_3^{2-} is the mobile ion that throughs the MCFC membrane:



In MCFC, CO_2 is produced at the anode and consumed at the cathode. Therefore, CO_2 must be extracted from the anode and recirculate to the cathode. Electrodes in a typical MCFC

are based on nickel that provides catalytic activity and conductivity. The optimum operation of this cell is around 650°C. It provides fuel flexibility because MCFC can run on hydrogen, methane and simple alcohols. The electrical efficiency of a typical MCFC is near 50%.

2.3.3.5. Solid oxide fuel cell

The SOFC uses a solid ceramic electrolyte. It is commonly used yttria-stabilized zirconia (YSZ), that is an oxygen ion conductor. The reactions at the anode and cathode are:



The fuel electrode must be able to withstand the reducing high-temperature environment of the anode and the air electrode must be able to withstand the oxidizing high-temperature environment of the cathode. The material for the cathode is usually a mixture of ceramic materials with good ion-conducting and electronically conducting properties. The material for the anode electrode is a nickel-YSZ cermet. The operating temperature of the SOFC is between 600 and 1000°C. It makes that the materials requirements more difficult. By the other hand, SOFC has fuel flexibility, and a high efficiency about 50-60%.

It can be seen in the Table 2.2. a comparison summary of them. Among the primary fuel cell types described, PEMFCs and SOFCs offers the best efficiencies and power density, so that, they have the best prospects to continue with their development. Due to their power range both the PEMFC and SOFC can be applied to residential power and other small scale stationary power applications. While SOFC can be used in high-power applications.

Table 2.2. Comparison Summary of the five major fuel cell types. Source: "Fuel cell fundamentals" by O'Hayre R. 2016. <https://onlinelibrary.wiley.com/doi/pdf/10.1002/9781119191766>

Fuel Cell Type	Electrical Efficiency (%)	Power Density (mW/cm ²)	Power Range (kW)	Internal Reforming	CO Tolerance	Balance of Plant
PAFC	40	150–300	50–1000	No	Poison (<1%)	Moderate
PEMFC	40–50	500–2500	0.001–1000	No	Poison (<50 ppm)	Low-moderate
AFC	50	150–400	1–100	No	Poison (<50 ppm)	Moderate
MCFC	45–55	100–300	100–100,000	Yes	Fuel	Complex
SOFC	50–60	250–500	10–100,000	Yes	Fuel	Moderate

2.3.4. Fuel Cell advantages

Fuel cells share some characteristics with combustion engines and batteries. In fact, fuel cells combine many of the advantages of both units. In the first place, fuel cells produce electricity directly from chemical energy and, in contrast, combustion engines first convert chemical energy into heat, then mechanical energy, and finally electricity. It means that fuel cells are more efficient than combustion engines. Secondly, fuel cells allow easy independent scaling between power and capacity. The power is determined by the fuel cell size and the capacity is determined by the fuel reservoir size. Unlike batteries, where power and capacity are intertwined. Also, fuel cells have not moving parts. It means that fuel cells are silent. Finally, as has been discussed previously, fuel cells are harmful emission free.

2.3.5. Main applications of Fuel Cells

Any application that requires electric energy is a potential application for fuel cells. Usually, fuel cell applications are divided into three areas: portable power, stationary power and transportation.

2.3.5.1. Portable power

Portable fuel cell systems are important in the market of electronic devices such as cellular phones or laptop computers. For this type of applications, it is necessary high-power densities, small sizes and simplicity. They compete directly with batteries and they will be successful depends on several considerations: fuel cells can be made small enough to fit inside portable electronic devices, the price is attractive enough and the replacement fuel cartridges are readily available (Hoogers, 2003).

2.3.5.2. Stationary power

Stationary power systems are compatible with other conventional and renewable primary power sources to create an optimal energy system that can be used to fill intermittency gaps of energy supply. With regard to off-grid applications, fuel cells are able to continuously operate over long periods where fuel is available and can be installed in sensitive environment where low emissions and low noise are required. Moreover, fuel cells

are often implements as part of a combined heat and power (CHP) system, also known as cogeneration, where the thermal energy from the fuel cells exhaust is recovered and cab be used to heat. (U.S. Department of energy, 2017).

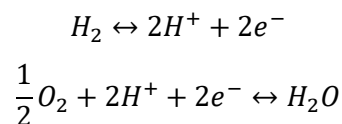
2.3.5.3. *Transportation*

The transportation sector constitutes one of the most important application for fuel cells. Fuel cells can be used for many transportation applications including automobiles, buses, utility vehicles, scooters and bicycles. What makes fuel cells attractive for transport applications is the fact that they emit zero emissions. And this is what inspired automotive companies in the 1980s and 1990s to start developing fuel-cell-powered cars and buses. For example, the hydrogen bus from Skoda Electric company and the car powered by PEM FC from Honda company. But, fuel cells need additional devices to provide the power needs to for acceleration and deceleration of vehicles.

2.4. PROTON EXCHANGE MEMBRANE FUEL CELL (PEM FC)

2.4.1. PEM FC principle

The PEMFC has numerous advantages like a high-power density, high energy conversion efficiency, fast startup and environmental friendship (Zhang & Wu, 2013). It uses as electrolyte a proton-conducting membrane, usually a perfluorinated polymer such as Nafion. This Nafion membrane helps to conduct protons from the anode to the cathode and also separates the anode from the cathode. The reactions in PEMFC are:



The whole process of a H₂/air PEM fuel cell produces electricity, water and heat, without any polluting byproduct.

In H₂/air PEM fuel cell, the Hydrogen Oxidation Reaction (HOR) and the Oxygen Reduction Reaction (ORR) take place in the anode and cathode Catalyst Layer respectively. In

a single fuel cell there are also two pieces of Gas Diffusion Layer located on either side of the membrane that are coated with a thin layer of platinum-based. This anode GDL, anode CL, membrane, cathode CL, and cathode CDL structure is referred as a membrane electrode assembly (MEA) (O'Hayre & Suk-Won, 2016) and it is the most important part of a PEMFC.

2.4.2. Elements of a PEM Fuel Cell

A single PEMFC is formed by the MEA, flow field bipolar plate, current collector, as well as other components like sealing materials and the end plate as can be seen at Figure 2.15. The following sections will describe these components separately.

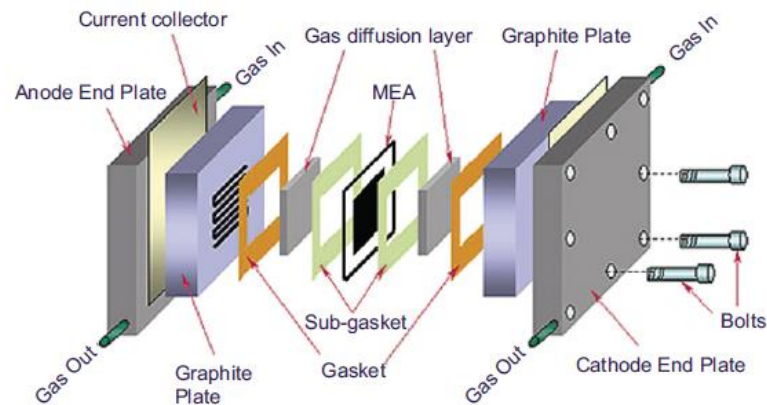


Figure 2.15. The structure of a typical PEM fuel cell. Source: "Electrochim Acta" by Lim, C., Wang, CY. 2004; 19:4149-56.

2.4.2.1. Fuel Cell Electrocatalysts

To date, the most active and widely employed catalyst in PEMFC is dispersed Pt-based catalyst. During the previous decades, many kinds of Pt-based electrocatalysts have been developed for ORR. These include Pt and Pt-based binary alloy catalysts, such as PtFe, PtCo, and PtNi. Normally, these catalyst particles are dispersed on supports with a bigger particle sizes to increase the active surface area. The most commonly used supports are carbon materials, which have large surface areas and good electronic conductivity as well as relative chemical and thermal stabilities. The widely used carbon support materials are carbon blacks. However, one drawback of such carbon supports is their electrochemical instability (called

carbon corrosion) under PEM fuel cell operating conditions. Carbon support corrosion causes Pt catalyst particle isolation and CL deactivation, which results in fuel cell performance degradation.

2.4.2.2. Catalyst layer

Cathode and anode CLs are a thin layer (usually $<50\mu\text{m}$) composed of catalyst powder, proton conductive ionomer such as Nafion and polytetrafluoroethylene (PTFE) as binder. PTFE also provides a suitable hydrophobicity to avoid water flooding. An ideal CL provides passages for proton transport, electron transport, reactant gas transport and should be able to remove product water but, at the same time, water is required to maintain the proton conductivity of the Nafion. So, it is necessary to reach an agreement between both necessities.

The reaction in PEMFC have three phases, involving the reactant gases, proton conductive ionomer and electron conductor (carbon-supported Pt catalyst), as can be seen in the Figure 2.16.

The key requirements for the catalyst layer include: high catalytic activity, high surface area/high density of triple-phase boundaries, high stability, ionic conductivity, minimal degradation and low cost. These important properties of CL are determined by its structure, fabrication method, and the composition ratio of Nafion and Teflon respect to de carbon amount. How influence these ratios in fuel cell performance and achieve the best composition is one of the main goals of the present thesis.

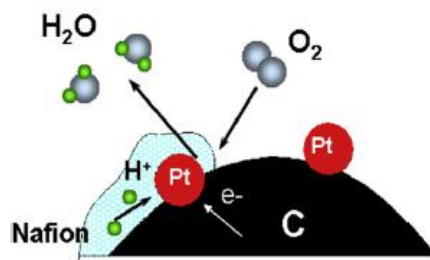


Figure 2.16. Schematic of a three-phases reaction boundary. Source: “PEM Fuel Cell Testing and Diagnosis” by Zhang, J. and Wu, J.

2.4.2.3. Gas diffusion layer

This layer is the thicker, protective second layer of the fuel cell electrode structure. The gas diffusion layer or GDL must protect and provide of electrical connectivity the catalyst layer, while permitting gas to diffuse into the CL. GDL also plays a role in the removal of liquid water from the fuel cell. A material chosen for GDL should have the next requirements: high electrical conductivity, high gas permeability, high corrosion resistance, facilitation of water removal, good mechanical properties and low cost. One of the most common GDL material that exhibits all the properties listed above is the carbon paper and the carbon cloth.

A common practise is to improve the interface between the GDL and de CL by applying an intermediate Microporous Layer (MPL). It consists of carbon or graphite powder with a hydrophobic material like Teflon as a binder that are spraying onto the GDL. This microporous layer provides a transition between large scale porosity (10-30 μm pores) of the GDL and the fine scale porosity (10-100 nm) of the catalyst layer, preventing the catalyst ink from penetrating in GDL. MPL also improves the water management, redistribute the reactants and reduce the contact resistance between the GDL and the CL, reducing the internal resistance of the PEMFC.

2.4.2.4. Membrane

The membrane works as PEMFC electrolyte and it is based on thin polymeric materials. Membrane must conduct protons but not electrons, be gas impermeable to prevent the mixing of anode and cathode gases and be as thin as possible to minimize the resistance. The most extensively used Proton Exchange Membrane in PEMFC is the perfluorosulfonic acid membrane such as Nafion. This electrolyte material is intimately involved in the ionic transport and it is extremely sensitive to the level of hydration. Because of that, operation temperature is restricted below 100 $^{\circ}\text{C}$ and usually, hydration is achieved by humidifying the fuel and the oxidant gases.

2.4.2.5. Membrane Electrode Assembly

The seven layers described above can be seen in the Figure 2.17. They are: anode GDL, anode microporous layer, anode catalyst layer, membrane, cathode catalyst layer, cathode microporous layer, cathode GDL and they together resulting in the Membrane Electrode Assembly or MEA. Hot pressing process is an effective and simple way for assembling electrodes and the membrane.

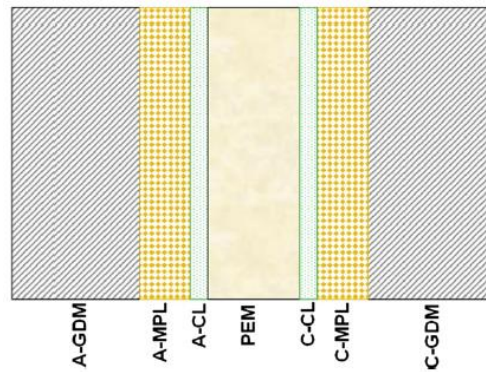


Figure 2.17. Schematic structure of MEA. Source: “PEM Fuel Cell Testing and Diagnosis” by Zhang, J. and Wu, J.

2.4.2.6. Bipolar plates

Flow field plates are elements located in the end of a single fuel cell. These plates have two main functions. Firstly, they must distribute fuel and oxidant to anode and cathode respectively and secondly, they work as current collector plates allowing the connexions among single fuel cells connected in series. Bipolar plates are usually made of graphite into which flow channels are conveniently machined. Alternatives to graphite include corrosion-resistant metals such as stainless steel. The main properties of a flow field plate are: high current conduction, high heat conduction, good control of gas flow and good product water removal.

The shape, size and pattern of flow channels can significantly affect the performance of a fuel cell. A poor design flow field plate can flood certain regions with liquid, thus blocking gas access and reducing the output current of the cell. There are three basic flow patterns: parallel flow, serpentine flow and interdigitated flow. Figure 2.18 shows that.

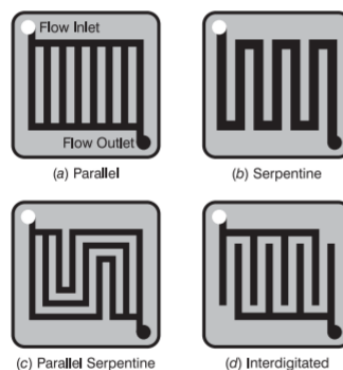


Figure 2.18. Major flow channel geometries. Source: “PEM Fuel Cell Testing and Diagnosis” by Zhang, J. and Wu, J.

2.4.3. Fuel Cell Performance

The performance of a fuel cell is summarized at graph in the Figure 2.19. This figure shows the voltage output for a given current output. In practice, the actual voltage output is less than the ideal thermodynamically predicted voltage. Furthermore, the more current that is drawn for a real fuel cell, the lower voltage output of the cell, limiting the power delivered.

The power density curve is produced by multiplying the voltage by the corresponding current density at each point. The current supplied by a fuel cell is proportional to the amount of fuel consumed. Therefore, as fuel voltage decrease, the electric power produced per unit of fuel also decreases. So, voltage can be seen as a measure of fuel cell efficiency. The real voltage output is less than predicted due to three major types of losses:

- Activation losses due to the electrochemical reaction.
- Ohmic losses due to ionic and electronic conduction.
- Concentration losses due to mass transport.

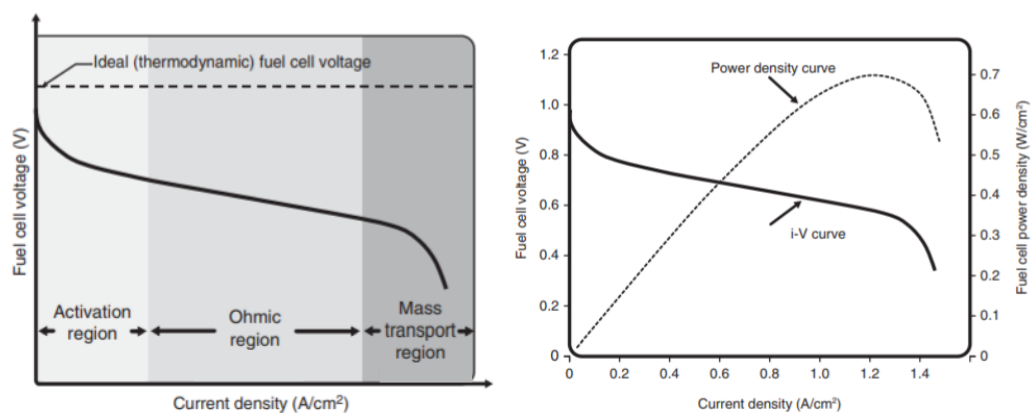


Figure 2.19. Schematic of fuel cell i-V curve (right). Combined i-V curve and power density. Source: “PEM Fuel Cell Testing and Diagnosis” by Zhang, J. and Wu, J.

Activation losses can be minimized rising the operation temperature of the fuel cell. However, the humidity of the membrane decreases, and the ionic conductivity also falls. Activation losses can be reduced using more efficient catalysts, rising the concentrations of reactants and increasing the operating pressure.

Ohmic losses are mainly produced by the proton transport resistance through the membrane that depends on its hydration.

Losses due to mass transport happens at high current densities due to the slow diffusion of gases into the electrode pores, the diffusion of reactants and products through the electrolyte and the cathode flood produced when water removal is not enough.

2.4.4. Fuel cell stack

A fuel cell stack consists of a many single cells connected in series. The electronic series connection of all these single cells is realized by the electronic conducting bipolar plates. A bipolar plate simultaneously acts as anode of one cell and cathode of the neighbouring cell, see Figure 2.20. The power generation is determined by the number on cells and the single cell performance.

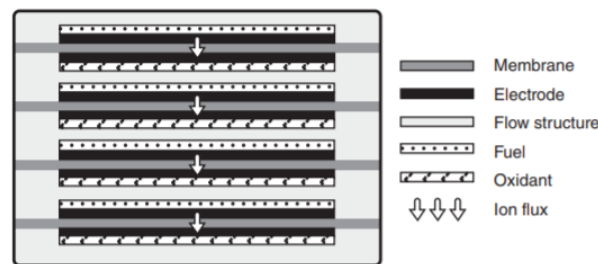


Figure 2.20. Vertical stack interconnection. Source: “PEM Fuel Cell Testing and Diagnosis” by Zhang, J. and Wu, J.

3. EXPERIMENTAL DESIGN

The goal of this master thesis is find a PEMFC catalyst with a high-power density reducing the amount of platinum content. The experimental process to know how powerful the catalysts are can be divided into three major parts: ink formulation, ink deposition, and fuel cell assembly and testing. Figure 3.1 shows the block diagram about the process. Every main step is marked with a different colour.

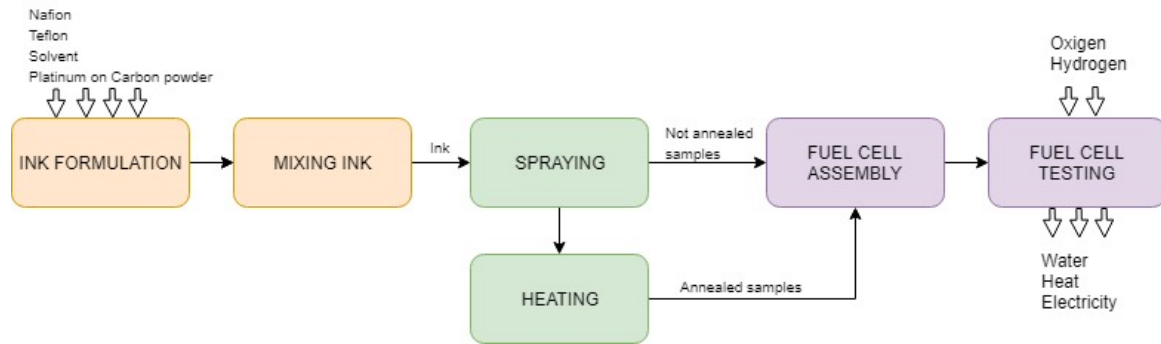


Figure 3.1. Process block diagram. Source: own elaboration.

3.1. INK FORMULATION

Catalysts has been formulated mixing carbon powder that contains ultra-small platinum particles with Nafion 5% w/w in water and 1-propanol (Alfa Aesar), Teflon and isopropanol as solvent, see Figure 3.2. The strategy for preparing the different catalyst is based on the combination of different ratio of Nafion/C and Teflon/C and four different catalyst powders:

- 30 % Platinum on carbon. (FuelCellStore).
- 40% Platinum on carbon. (FuelCellStore).
- 60% Platinum on carbon. (FuelCellStore).
- 60% Platinum on carbon High Surface Area Ketjenblack. (FuelCellStore).

The rate of Nafion studied has varied from 0 to 1.75 for platinum on carbon 40% and ratio 0.3 teflon/C and the ratio of Teflon studied rises from 0 to 0.6 for a ratio of Nafion about 0.8 and for platinum on carbon 40%.



Figure 3.2. Ink compounds. Left to right: teflon, isopropanol, nafion, catalyst powder.

Below, it is described as example the calculation method to know the necessary amount of each compound for an ink with the composition: 1C + 0.428 Pt + 0.8 N + 0.3 T.

Data:

60 mg Pt/C 30 %

20 ml IP

5% w/w of nafion

Nafion solution density (5°C): 1.08537 kg/l

55% w/w teflon

Teflon solution density (20°C): 1.4 kg/l

Content of nafion

Mass of C: $60 \text{ mg} \cdot 0,7 = 42 \text{ mg}$

Mass of N: $42 \text{ mg} \cdot 0,8 = 33,6 \text{ mg}$

Mass of solution (5% w/w of nafion): $33,6 \text{ mg} / 0,05 = 672 \text{ mg}$

Volume of solution (Mass of solution / density of solution): $672 \text{ mg} / 1,08537 = 619,143 \text{ } \mu\text{l}$

Content of teflon

Mass of C: $60 \cdot 0,7 = 42 \text{ mg}$

Mass of T: $42 \text{ mg} \cdot 0,3 = 12,6 \text{ mg}$

Mass solution (55%w/w of teflon): $12,6 \text{ mg} / 0,55 = 22,91 \text{ mg}$

Volume of solution (Mass of solution / density of solution): $22,91 \text{ mg} / 1,4 = 16,36 \text{ } \mu\text{l}$

When the composition is known, all the components are mixed manually (see Figure 3.3 left) and after, the suspension is prepared by ultrasonic dissolving for 10 minutes (see Figure 3.3 right).



Figure 3.3. Ink (left) and ultrasonic mixed (right).

3.2. INK DEPOSITION

3.2.1. GDL preparation

When the ink is ready. It is necessary to prepare the pieces of GDL that will be coated. The ink support used is carbon fiber paper (Singracet 29 BC) with a thickness of 235 microns and 80% of porosity. This GDL has a treatment with teflon in order to make the material hydrophobic and improve the water transport. The GDL also has a microporous layer (MPL) on one side that minimize the contact resistance between the GDL and the catalyst layer. The pieces are cut into squares 40x40 mm and after, all are weighed.

3.2.2. Sonicated spraying

Next step consists of spraying the ink onto the GDL using Sono-Tek machine. This is a coating machine that has the ability to deposit very uniform nanolayers of material. Sonicated spraying is a novel technique based on ultrasonic and sonoelectrochemical devices (Bladergroen & Su, 2012). In the process, the catalyst ink is first inserted in a sonicated syringe. Later, all the parameters of the machine must be configured:

- Temperature: 65°C.
- Path speed: 5 mm/sec.
- Tool on wait: 0.04 s.
- Tool of distance: 0 mm.
- Area spacing: 5mm.
- Fast area: arcs.

After this, the GDL piece is collocated on the heat plate and then, liquid is atomized through the nozzle into a fine mist using high frequency sound vibrations. The platinum loading is calculated by weight differences (before and after spraying). Various passes are necessities to obtaining the platinum loading desired (0.07, 0.1, 0.2, 0.3 mg Pt/cm²). Figure 3.4 shows the experimental design of sonicated machine.

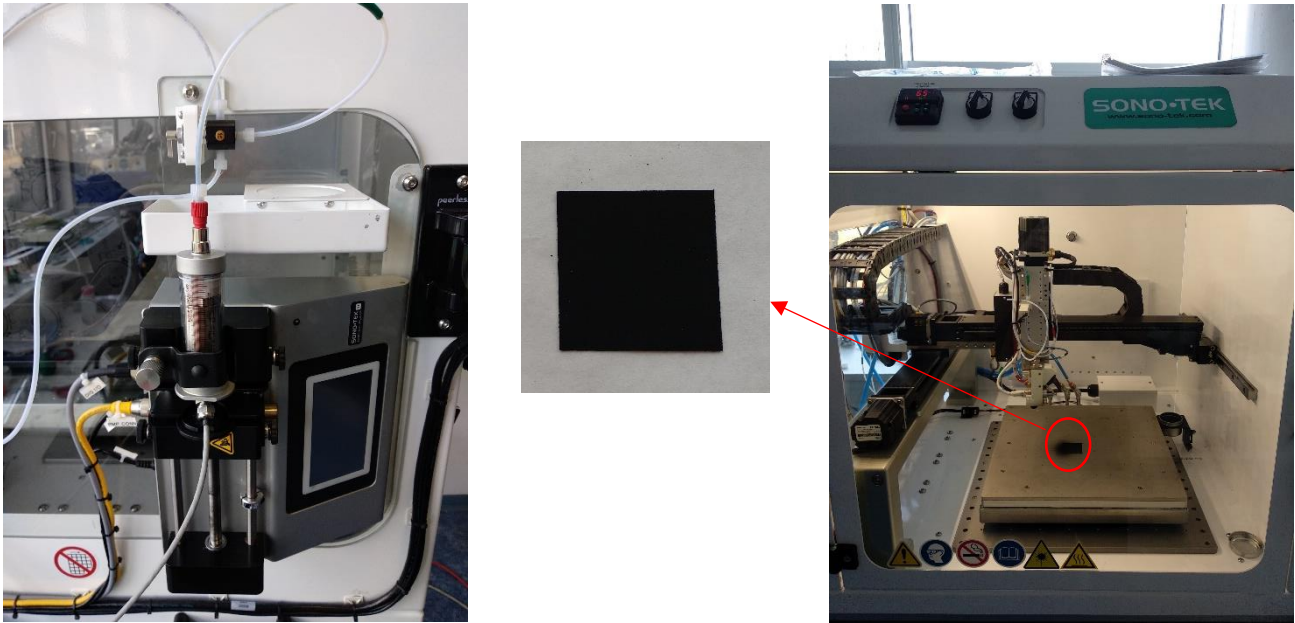


Figure 3.4. Syringe with ink (left), GDL (middle), Sono-tek machine (right).

3.2.3. Heating of the samples

The following step is heating the samples. For the purpose of knowing how the heat has influence on the samples, the big piece (40x40 mm) is divided into 4 square parts of 20x20 mm. After this, two pieces are baked in the oven during 2 hours at 150°C. The other two will be used to compare the different power density achieved by annealed and not annealed samples.

3.3. FUEL CELL CHARACTERIZATION TECHNIQUES

3.3.1. Fuel Cell Assembly

Single fuel assembly is the process of putting together all the components that requires a fuel cell. In this work has been used two graphite plates as a gas distributor, two sealing gaskets and the MEA. Figure 3.5 shows the components of the assembly with an active area of 4 cm².



Figure 3.5. At right it is seen one graphite plate and left, MEA on top of the other graphite plate. On green and white the gaskets.

3.3.2. Fuel Cell Testing

There are different fuel cell characterization techniques. In this thesis has been used an electrochemical characterization technique (in situ). This method uses the electrochemical variables of voltage, current, and time to characterize the performance of fuel cell device under operating conditions. It is seen in the Figure 3.6 that the power increases up to a maximum with decreasing cell voltage. This system draws a fixed current front the fuel cell and measures the corresponding output voltage.

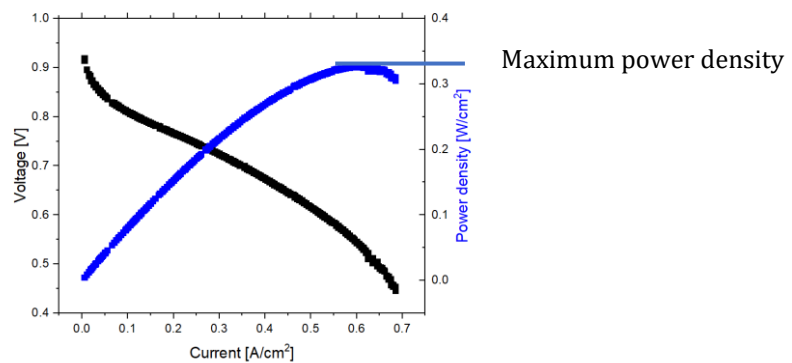


Figure 3.6. Relation between power and cell voltage.

The image of the experimental setup for fuel cell testing is shown in Figure 3.7. Gases are humidified before going inside the cell and pressure is regulated in the working point. The temperature is also controlled by PID controller and set at the working point. Fuel cells are pressurized by a piston. The Fuel cell has connection with four gas flows: oxygen, hydrogen, air and nitrogen.

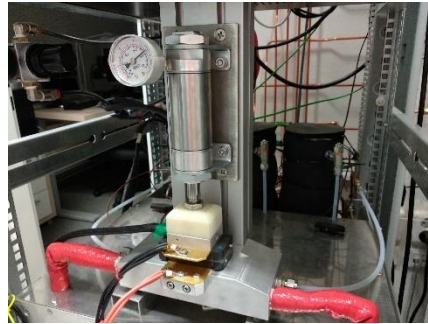


Figure 3.7. Station for testing PEMFC.

It is important considerer the test conditions and they should be carefully controlled. The conditions for the testing used in the present thesis are controlled by computer with a software already developed, see Figure 3.8. Fuel cells have worked under the next operation conditions:

- Temperature of fuel cell, gas inlet and exits: $\sim 70^{\circ}\text{C}$.
- Gas pressure: 0.5 bar.
- Compression force of the fuel assembly: 8 bar.
- Flow rate: 0.5.
- Fixed-stoichiometry condition (ratio between the reactant supply and current consumption is always fixed):
 - H_2/O_2 fuel cell:
 - Anode: 1.2
 - Cathode: 2
 - H_2/Air fuel cell:
 - Anode: 1.2
 - Cathode: 15

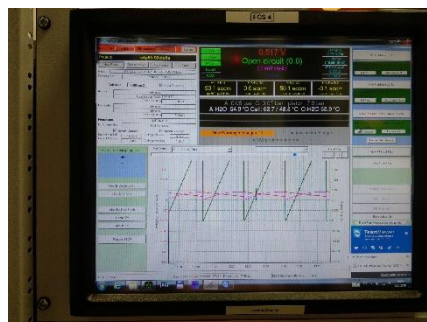


Figure 3.8. Software for control operational conditions.

4. EXPERIMENTAL RESULTS AND DISCUSSION

In this section are exposed and discussed the experimental results obtained about the power density of every catalyst. In particular, it is studied one operating parameter of sono-tek machine, specifically, the height at which nozzle sprays the ink. Also, it has been observed the difference between use GDL and n-GDL and how the ink is deposited on the top. The influence about the porosity of the carbon powder that contents the platinum particles. And it is discussed the influence of the ratio of nafion/carbon content, the amount of teflon in the ink, the differences between annealed and not annealed samples, how influence the type of catalyst powder used in the power density and, finally, the behaviour of the power density related to the platinum loading.

4.1. EFFECT OF SPRAYING NOZZLE HEIGHT

With the aim of knowing the influence of the spraying nozzle height, three samples have been sprayed with the same ink and it has been achieved the same platinum loading for three different heights. Sample 1z0 has been sprayed at the maximum height that sono-tek machine allows, 1hz75 has been sprayed at minimum height and 1hz40 has been sprayed in an intermediate height. The best results are obtained by 1hz75, the sample spraying at lowest height. The power density for H₂/Air fuel cell and H₂/O₂ fuel cell is 0.41 W/cm² and 1.08 W/cm², Table 4.1 summarizes the results.

The number of spraying cycles to achieve the 0.16 mg/cm² of platinum loading is different in depend of the nozzle height. The sample with worst power density needed 28 cycles, 7 times more than the sample with the highest power density. So, it means that the largest number of cycles could have influenced the thickness of the sample, making it thicker and, as consequence, the diffusion of gasses is worst, the chemical reactions are slower, and the power density decreases.

Table 4.1. Effect of the spraying nozzle height.

Sample	Pt loading [mg/cm ²]	Power Density [H ₂ /O ₂] [W/cm ²]	Power Density [H ₂ /Air] [W/cm ²]	Cycles
1hz0 (max)	0.16	0.74	0.37	28
1hz40	0.16	0.8	0.39	8
1hz75 (min)	0.16	1.08	0.41	4

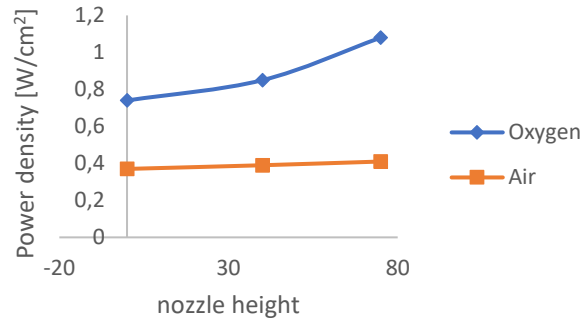


Figure 4.1. Effect of spraying nozzle height.

Due to the results, it was decided that all the other samples were prepared at lowest nozzle height to save time, materials and to obtain better power densities.

4.2. DIFFERENCES BETWEEN n-GDL AND GDL

The difference between GDL and n-GDL is that the second one has a Microporous Layer that provides better properties to the GDL. It can be seen in Figure 4.2 how the pores of GDL (left) are more open and the catalyst is penetrating the carbon support. In that case, when GDL is sprayed, it is not possible to create a homogeneous catalyst layer, impeding an efficient contact among reactants and the platinum. In contrast, SEM image of n-GDL shows a better dispersion of platinum along a continue layer of catalyst.

The power density obtained by the GDL sample is lower than 0.1 W/cm^2 using pure oxygen and the power density obtained by the n-GDL sample is 0.76 W/cm^2 for pure oxygen and 0.1 W/cm^2 for air. In comparison, n-GDL is significantly better. Owing to this result, it was decided to continue the researching just using n-GDL.

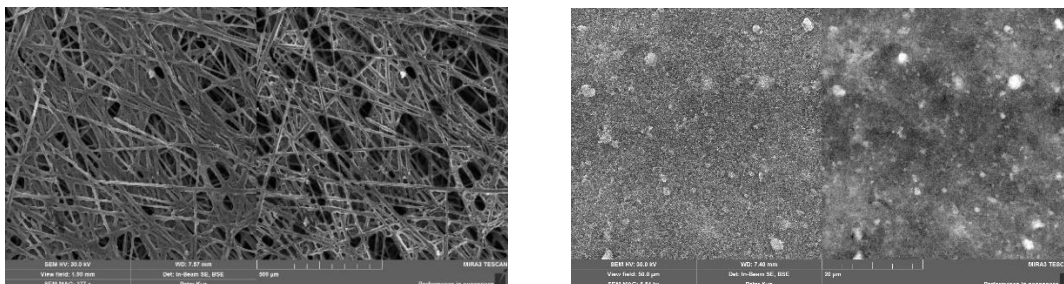


Figure 4.2. SEM image GDL (right) and SEM image n-GDL (left). Ink used is $1\text{C} + 1.5\text{Pt} + 1.75 \text{N} + 0.3 \text{T}$ and 0.1 Pt loading.

4.3. EFFECT OF THE CARBON POROSITY

The parameter that has been investigated in this section is related to the porosity of carbon powder where the platinum is supported. Figure 4.3 shows SEM images about 60% platinum on non-porous carbon powder (left) and 60% platinum on porous carbon Ketjenblack powder (right). Porous carbon achieves a better dispersion of platinum while non-porous carbon shows parts with platinum clusters (highlighted in red) and other parts with a reduced presence of platinum. Power density of sample with porous carbon is practically twice higher than non-porous power density, as Table 4.2 shows.

For a platinum loading of 0,1 mg/cm², power density is 0.56 W/cm² with non-porous carbon and 0.9 W/cm² with porous carbon while for a platinum loading of 0.2 mg/cm² the power densities are 0.4 W/cm² and 0.87 W/cm² for non-porous carbon and porous carbon respectively. As opposed that could be thought, the power density doesn't increase with more amount of platinum and in case of non-porous carbon, the power density falls more than for porous carbon, probably because for higher amounts of platinum, clusters are bigger and the real active surface decreases.

So, it stands to reason that, for the same platinum loading, platinum in porous carbon sample is better dispersed and because of that it has more contact with the reactants and can produce a higher power density.

Table 4.2. Comparison between samples with platinum on porous and non-porous carbon powder.

Type of Pt catalyst	Pt loading [mg/cm ²]	Power Density [H ₂ /O ₂] [W/cm ²]	Power Density [H ₂ /Air] [W/cm ²]
Pt/C60	0.1	0.56	0.18
Pt/C60Ket.	0.1	0.9	0.29
Pt/C60	0.2	0.4	0.15
Pt/C60Ket.	0.2	0.87	0.29

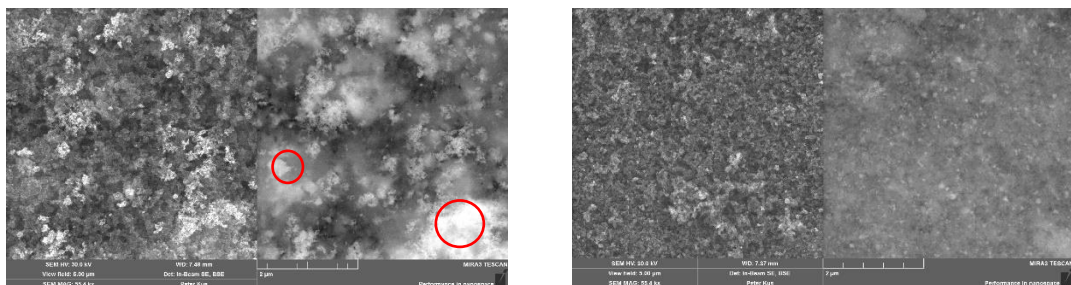


Figure 4.3. 60% Pt on carbon (left) and 60% Pt on porous carbon.

4.4. EFFECT OF THE TEFLON CONTENT

The goal of this part of the work is directly related to the composition of the ink, particularly, to the amount of teflon regarding the carbon content. For study his influence in the performance of the fuel cells has been prepared three samples with the same platinum loading (0.1 mg/cm^2), the same type of catalyst powder (40% platinum on carbon) and the same ratio Nafion/Carbon (0.8), but with different Teflon/Carbon ratios.

The worst power density is obtained for the ink without teflon as can be seen in the Table 4.3, with result of 0.5 W/cm^2 for H_2/O_2 and 0.23 W/cm^2 for H_2/Air . It is expected because, although teflon has not a direct influence on the PEMFC chemical reactions, teflon is a hydrophobic agent that helps to remove water. When there is not teflon, water flooding occurs and the passages in the catalyst layer are limited. As consequence, the gas transport decreases and also, the speed of the chemical reactions and the power density.

The results for the ratio of 0.3 and 0.6 are quite similar when it is used air as oxidant. But when it is used pure oxygen, the best power density is for the ratio 0.3. This behaviour is expected because more amount of teflon roses the removal of water and it has a negative impact in the activation of the Nafion membrane. The membrane needs to be humidified for achieve a high proton conductivity and as result, there is a direct dependence between the proton conductivity of the membrane and the water content. Consequently, some compromise between prevent the inundation of the electrode and achieve a high proton conductivity is necessary.

Due to these results, the ink used to analyse the other parameters has had a ratio of Teflon/Carbon of 0.3. It is important to note that this result is only valid for the fuel cell operating conditions used. In another unit, with different temperatures, pressures or humidifying system the optimum amount of teflon can change.

Table 4.3. Power density for different content of teflon.

Content of teflon [T/C]	Power Density [H ₂ /O ₂]	Power Density [H ₂ /Air]
0	0,5	0,23
0,3	1	0,29
0,6	0,91	0,3

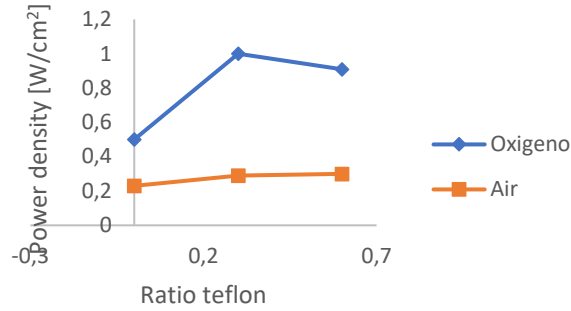


Figure 4.4. Power density for different ratio Teflon/Carbon (0, 0.3 and 0.6).

4.5. EFFECT OF THE NAFION CONTENT

The study of the influence of the content of Nafion in the ink has been one of the main targets of this thesis. Nafion is one of the three phases among the chemical reaction happens in the catalytic layer. Because of that, it has been studied the power density obtain with catalysts that contains different ratios of Nafion/carbon. All the inks have the same teflon/carbon ratio (0.3) and they are prepared with 40% of platinum on carbon powder. The platinum loading achieve for this study is $\sim 0.1 \text{ mg/cm}^2$.

It is easy to observe in Figure 4.5. **Influence of ratio Nafion/Carbon.** that the power density peaks at ratio of 1.2 Nafion/carbon, with values of 1.2 W/cm^2 and 0.4 W/cm^2 for H_2/O_2 and H_2/Air fuel cells respectively. In the case of H_2/Air fuel cells, the power density is gradually increasing until the maximum value and after, power density decreases steadily. By contrast, the power density of H_2/O_2 fuel has not the same steady evolution. For Nafion/carbon 1 and 1.5 the power density is lower than expected. Even so, the best ratio Nafion/carbon is 1.2.

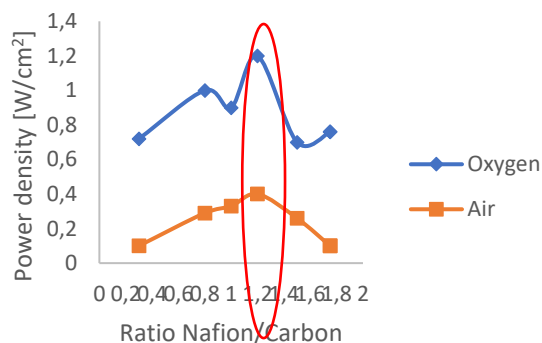


Figure 4.5. Influence of ratio Nafion/Carbon.

The power density rises proportionately to the amount of Nafion because the three phases reaction area increase, and this optimizes the fuel cell performance. However, an excess of nafion may wrap around the platinum particles and deactivate it. This may be the reason why power density falls for the ratio of 1.5 and 1.75.

The content of Nafion has influence the structure of the sample, making it more porous. In that case, the dispersion of particles improves, and it increases the catalyst active area and the final performance of the fuel cell. Table 4.4 shows all the results for every amount of Nafion.

Table 4.4. Effect of the ratio Nafion/carbon.

Pt loading [mg/cm ²]	Content of Nafion [N/C]	Power Density [H ₂ /O ₂]	Power Density [H ₂ /Air]
0.13	0.3	0.72	0.1
0.1	0.8	1	0.29
0.11	1	0.9	0.33
0.12	1.2	1.2	0.4
0.1	1.5	0.7	0.26
0.1	1.75	0.76	0.1

4.6. INFLUENCE OF THE TYPE OF CATALYST POWDER

Platinum is the metal used as catalyst in the fuel cells and it is supported on carbon to maximize its surface area and activity. This catalyst powder can contain different percentages of platinum and carbon. In this work has been selected four different catalyst powders to prepare the catalyst ink: 30% Pt/C, 40% Pt/C, 60% Pt/C and 60% Pt/C Ketjenblack. The ink also has a ratio Nafion/Carbon 0.8 and a ratio Teflon/Carbon 0.3. Then, samples were sprayed until different platinum loadings (0.07, 0.01, 0.02 and 0.03), and tested to know the influence of the powder in the fuel cell power.

The results, as can be seen in Figure 4.6, it shows that 30% platinum on carbon power achieves the highest power density for 0.07 mg/cm², 0.1 mg/cm², 0.2 mg/cm² on both for H₂/Air fuel cell and H₂/O₂ fuel cell. Only for the platinum loading of 0.3 mg/cm², 40% platinum on carbon has the best power density.

Contrary to what could be expected, 30% platinum on carbon is the powder that provides the best power density and it can be consequence of its distribution on the carbon surface. The content of platinum on the powder is low, so that the distribution is better, the active surface increases and it permits the power density to rise. Moreover, the ink prepared with 30% Pt/C has less platinum concentration and due to this, samples requires more cycles to achieve the same platinum loading, it might help to obtain a better dispersion of platinum in the catalyst layer. By the other hand, 60% Pt/C has the worst power density results, probably because the platinum is worst distributed on the carbon particles due to a highest quantity. The platinum forms clusters that reduce the active area of the powder, the chemical reaction is slow and, due to that, the power density is smaller.

Figures also show that the order of powder efficiency is 30% Pt/C, 40% Pt/C, 60% Pt/C and 60% Pt/C Ketjenblack for all platinum loadings except 0.3 mg/cm². Again, it can be explained for the same reason discusses above, power density becomes worst as percentage of platinum on carbon increases and the activated area decreases. We can see it in Figure 4.7.

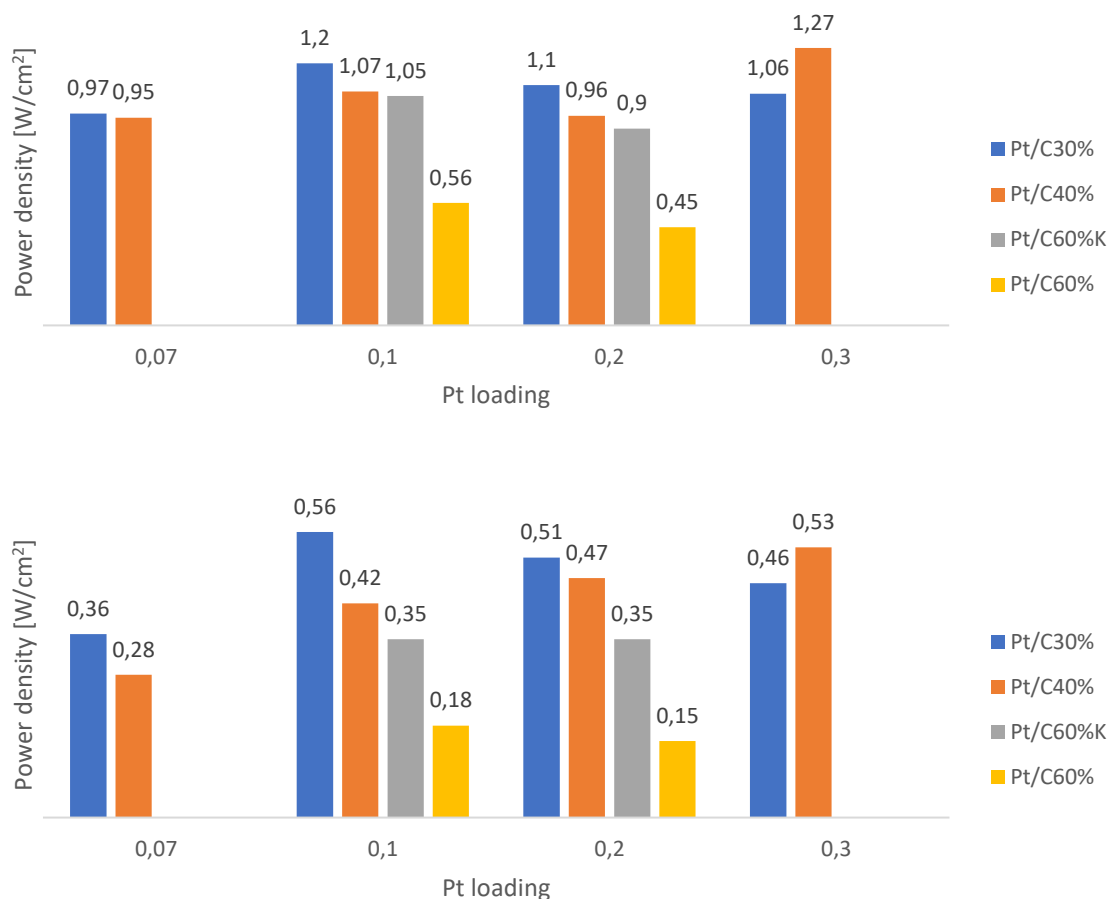


Figure 4.6. Power density of H₂/Air fuel cells (down) and H₂/O₂ (up) with a catalyst layer prepared with different catalyst power and with different platinum loading.

Worst results are obtained for 60% Pt/C, especially for powder with non-porous carbon. The reason is the same that has been discussed in section 4.3.

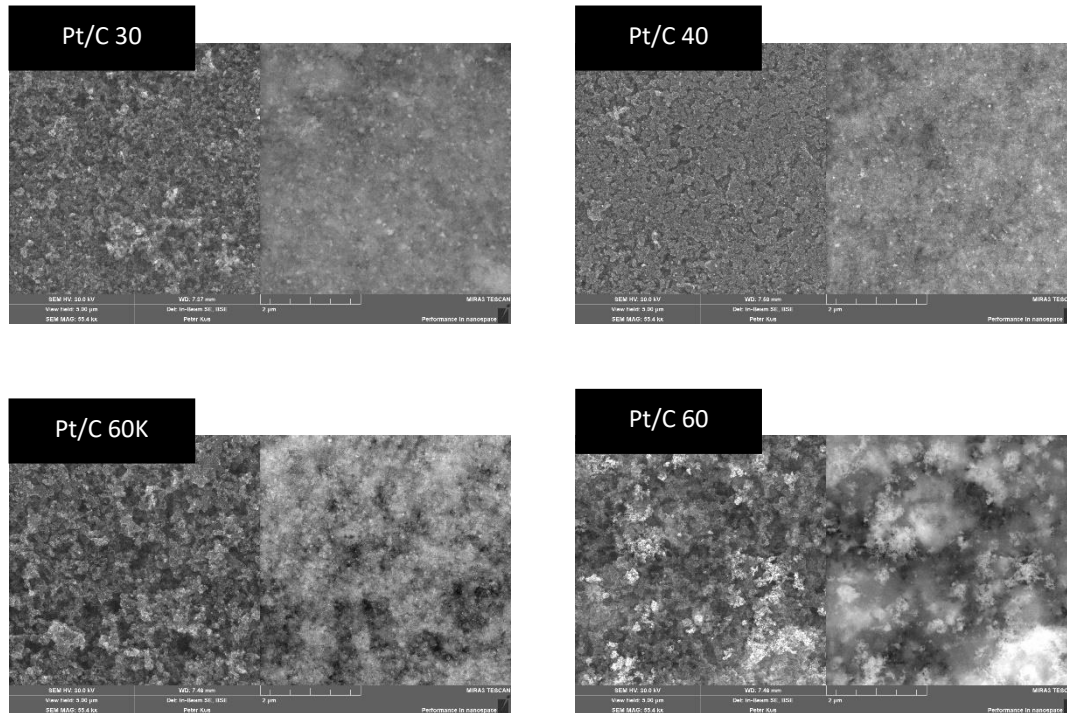


Figure 4.7. SEM images of catalyst powder with different percentage of platinum.

4.7. DIFFERENCES BETWEEN ANNEALED AND NOT ANNEALED SAMPLES

After spraying the catalytic ink onto the carbon support, performance of single fuel cells is tested. With the aim to maximize the power density produced by fuel cells, minimizing the amount of the platinum in the catalytic layer, some samples have been annealed. The annealing treatment consist of heating samples in the oven to 150°C for 2 hours.

In order to see how annealing influence on the performance of samples, it has been annealed and tested samples with 40% of platinum on carbon powder and a ration T/C 0.3. All the samples have a Pt loading of 0.1 mg/cm² and the ratio of N/C varies from 0 to 1.75. Table 4.5 shows the power density of annealed and not annealed samples. It can be observed that in all the cases, power density of annealed samples increases in comparison to not annealed. The improvement of power density, in average, is 48,31% for H₂/Air fuel cells and 20% for H₂/O₂ fuel cells.

These findings can be associated with a change in the catalyst layer structure due to the annealing. The solvent from the ink is completely evaporated and the structure becomes more porous, consequently, platinum can be more dispersed and the interfacial area between catalyst, Nafion and reactants enlarge producing an improvement of the catalyst efficiency.

Table 4.5. Power density of samples annealed and not annealed.

Ratio N/C	Not annealed		Annealed		% Improvement	
	Power Density [H ₂ /O ₂]	Power Density [H ₂ /Air]	Power Density [H ₂ /O ₂]	Power Density [H ₂ /Air]	Power Density [H ₂ /O ₂]	Power Density [H ₂ /Air]
0,3	0,72	0,1	0,93	0,15	29,17	50
0,8	1	0,29	1,07	0,42	7	44,82
1	0,9	0,33	1,04	0,36	15,56	9,09
1,2	1,2	0,4	1,31	0,51	9,17	27,5
1,5	0,7	0,26	1,05	0,36	5	38,46
1,75	0,76	0,1	0,83	0,22	9,21	120
					20%	48,31%

4.8. INFLUENCE OF PLATINUM LOADING

The effects of platinum loading on fuel cell performance are examined with platinum loadings of 0.07, 0.1, 0.2 and 0.3 mg/cm². The effect has been investigated for several inks composed by platinum on carbon 30%, 40% and 60%, with ratios of 0.8 N/C and 0.3 T/C.

On increasing the Pt loading from 0.07 to 0.3 mg/cm², the power density does not increase gradually. Samples with Pt loading of 0.1 mg/cm² always achieve a higher power density than for 0.07 mg/cm² Pt loading. But, Pt loading of 0.1 mg/cm² samples also produce more power density than 0.2 mg/cm² Pt loading samples in most cases, see Figure 4.8. **Power density for annealed and not annealed samples and different Pt loading (ink: Pt/C 60K, 0.8 N/C and 0.3 T/C)** Figure 4.8, Figure 4.9, and Figure 4.10. It is an unexpected fact, because twice amount of platinum should produce more power density. The higher performance of the single fuel cell using Pt loadings of 0.1 mg/cm² can be attributed to better platinum dispersion on the carbon support, increasing the catalyst active area, and a thinner catalyst layer with less gasses transport resistance that improves the chemical reaction and as result, also the power density.

Finally, with increasing Pt loading to 0.3 mg/cm^2 , power density of fuel cells rises slightly for 60% and 40% Pt on carbon inks, however this growth is 0.1 W/cm^2 in average in comparison with power density achieved with 0.1 mg/cm^2 Pt loading. The performance with 0.3 mg/cm^2 Pt loading is worst that could be expected in contrast to 0.1 mg/cm^2 Pt loading results. The performance was lowered probably due to the loss of catalyst active area produced by the agglomeration of platinum particles. By contrast, power density for 0.3 mg/cm^2 Pt loading in 30% Pt on carbon ink remains constant respect the power density produced by 0.1 mg/cm^2 Pt loading samples. These results suggest that catalyst layer with 0.1 mg/cm^2 Pt loading can obtain a high power density, similar to outcomes of 0.3 mg/cm^2 Pt loading but with a reduced amount of Platinum, making this catalyst suitable due to the decrease of platinum use and costs.

Table 4.6. Power density for annealed and not annealed samples and different Pt loading (ink: Pt/C 60K, 0.8 N/C and 0.3 T/C).

Pt loading	INK: 1C + 1.5Pt + 0.8N + 0.3T			
	Not annealed		Annealed	
	Power Density [H ₂ /O ₂]	Power Density [H ₂ /Air]	Power Density [H ₂ /O ₂]	Power Density [H ₂ /Air]
0.035	0.44	0.12	0.55	0.19
0.1	0.9	0.29	1.05	0.35
0.2	0.87	0.29	0.9	0.35
0.3	1.04	0.39	0.95	0.37

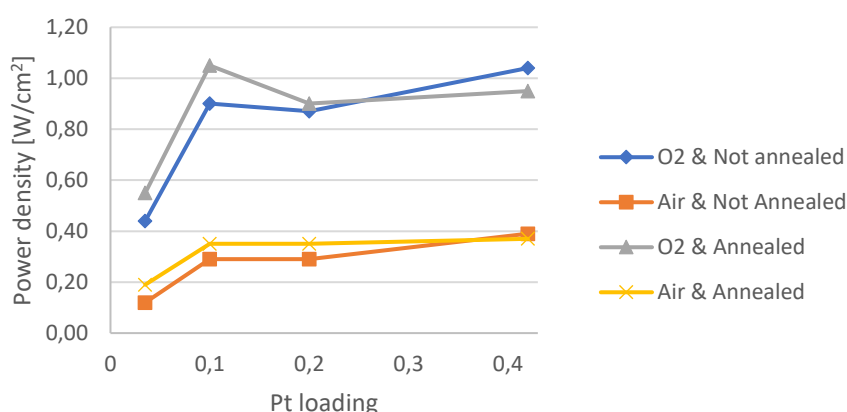
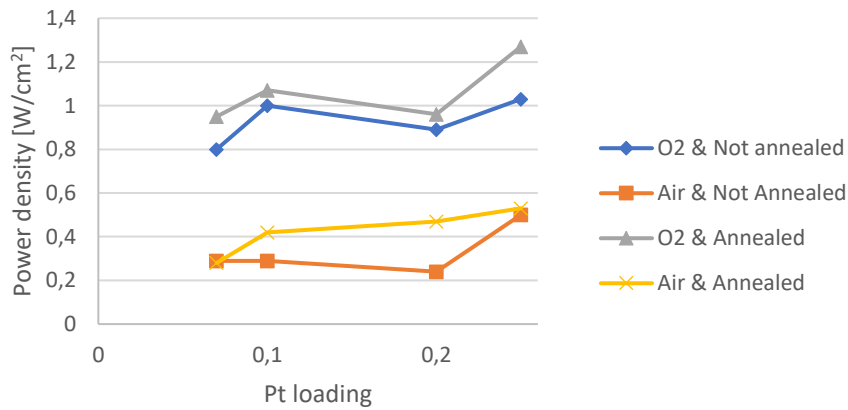


Figure 4.8. Power density for annealed and not annealed samples and different Pt loading (ink: Pt/C 60K, 0.8 N/C and 0.3 T/C)

Table 4.7. Power density for annealed and not annealed samples and different Pt loading (ink: Pt/C 40K, 0.8 N/C and 0.3 T/C)

Pt loading	INK: 1C + 0.67Pt + 0.8N + 0.3T			
	Not annealed		Annealed	
	Power Density [H ₂ /O ₂]	Power Density [H ₂ /Air]	Power Density [H ₂ /O ₂]	Power Density [H ₂ /Air]
0.07	0.8	0.29	0.95	0.28
0.1	1	0.29	1.07	0.42
0.2	0.89	0.24	0.96	0.47
0.3	1.03	0.5	1.27	0.53

**Figure 4.9.** Power density for annealed and not annealed samples and different Pt loading (ink: Pt/C 40, 0.8 N/C and 0.3 T/C)**Table 4.8.** Power density for annealed and not annealed samples and different Pt loading (ink: Pt/C 30, 0.8 N/C and 0.3 T/C)

Pt loading	INK: 1C + 0.428Pt + 0.8N + 0.3T			
	Not annealed		Annealed	
	Power Density [H ₂ /O ₂]	Power Density [H ₂ /Air]	Power Density [H ₂ /O ₂]	Power Density [H ₂ /Air]
0.066	0.95	0.37	0.97	0.36
0.12	0.97	0.35	1.2	0.56
0.2	0.95	0.46	1.1	0.51
0.31	1	0.4	1.06	0.46

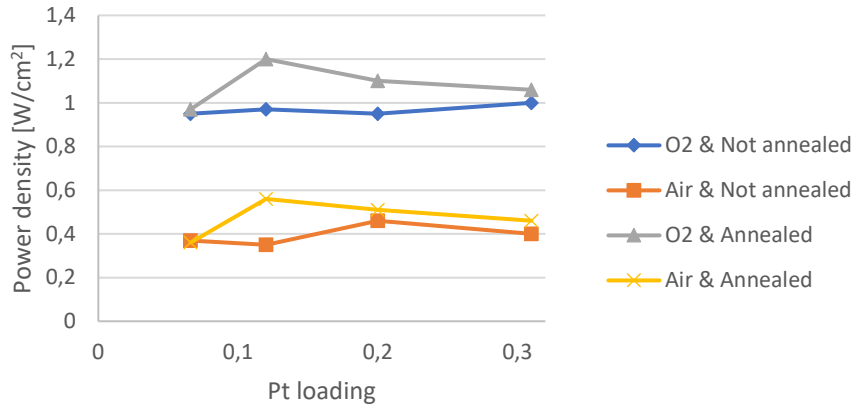


Figure 4.10. Power density for annealed and not annealed samples and different Pt loading (ink: Pt/C 30, 0.8 N/C and 0.3 T/C).

Among all these catalyst, there is one that has the best performance for both H_2/O_2 fuel cell and H_2/Air . It is the catalyst composed of 30% Pt/C, 0.8 N/C, 0.3 T/C and 0.1 mg/cm^2 Pt loading and the sample is annealed. Table 4.9 shows its composition and power density. The results for single fuel cell with pure oxygen as oxidant is $1.2 W/cm^2$ and the power density for the test with air is $0.56 W/cm^2$.

Table 4.9. Composition and power density about the best catalyst performance.

Pt/C	30%
Pt loading [mg/cm^2]	0,12
N/C	0,8
T/C	0,3
Power Density H_2/O_2 [W/cm^2]	1.2
Power Density H_2/Air [W/cm^2]	0.56

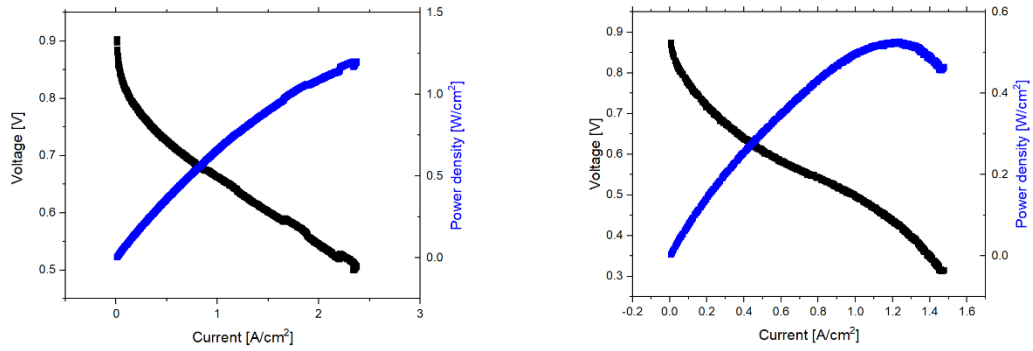


Figure 4.11. Power density curve for H₂/O₂ fuel cell (right) and power density curve of H₂/Air fuel cell (left).

These results are significantly better than the result for the commercial catalyst that obtains 1 W/cm² and 0.5 W/cm² for pure oxygen and air respectively but with the difference that it has a Pt loading of 0.3 mg/cm², three times more amount of catalyst. It makes our catalyst promising and nowadays, it is being testing in a stack composed by 14 single fuel cells and under real conditions, see Figure 4.12. **Stack formed by 14 fuel cells.**

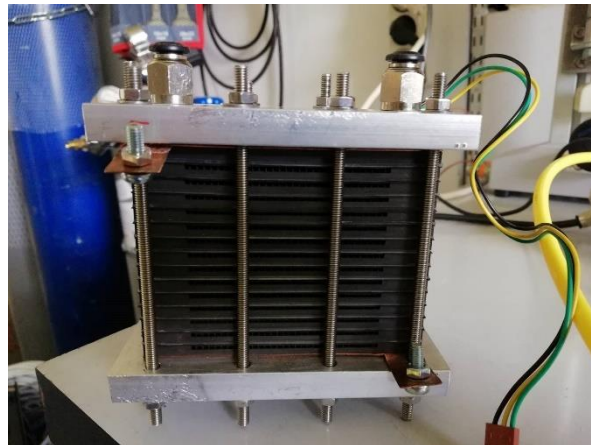


Figure 4.12. Stack formed by 14 fuel cells.

5. CONCLUSIONS

After the end of this work, it has shown that sono-tek machine can spray successfully platinum on carbon catalyst onto a n-GDL support and that one of the most important operational parameters of this machine is its spraying height. Spraying at the lowest height achieves better power density for the catalyst with less amount of platinum and in less time.

Furthermore, it has been selected the best material and parameters of design for obtaining the best catalyst possible. First one it is the benefits of use n-GDL instead GDL. n-GDL provides better power density due to its microporous layer, that helps to hold the catalyst layer and platinum particles has a good contact with reactant gases.

Moreover, samples were prepared with different ratio of Teflon and Nafion. The best power density was obtained for a ratio of N/C 1.2 and a T/C 0.3. The amount of Teflon is a compromise between the necessity of remove water to prevent electrode flooding and keep the Nafion membrane humidified. The ratio Nafion/Carbon with best power density results has been 1.2. This amount of Nafion increases the three phases reaction area, so that the amount of activate platinum rises.

Catalyst powder that produces better catalyst layer is 30% platinum on carbon, followed by 40% Pt/C, 60% Pt/C porous and 60% Pt/C. It is related with the carbon porosity and the dispersion of platinum on the carbon particle. Less amount of platinum benefits his dispersion and the activate surfaces area increases, improving the power of the catalyst.

Annealing process has proved to be beneficial to improve the performance of every catalyst. The samples annealed have a structure more porous that provides more functional distribution of platinum particles and as consequence the final power density grows.

Finally, catalyst layer with a platinum content of 0.1 mg/cm² and 0.3 mg/cm² has produced the highest power densities, growing up to 1 W/cm² and 0.5 W/cm² for H₂/O₂ fuel cell and H₂/Air fuel cell respectively. These results are better than commercial one, so that, both catalysts are promising, especially the catalyst with lower platinum amount because it would provide the accessibility to hydrogen technology to the scale production.

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