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MINI PASSIVE DIRECT METHANOL FUEL CELLS FOR PORTABLE APPLICATIONS

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Abstract

With carbon neutrality targets in mind, scientists and engineers are focused on finding more sustainable technologies. Fuel cells, and more specifically, the mini passive direct methanol fuel cells (mpDMFC), emerged as a way of producing sustainably electric energy in portable devices such as hearing aids and mobile phones. However, commercialisation of these cells is still in early stages, mainly due to the cost associated with the catalysts, platinum-based, and loadings used.

The main objective of this dissertation was to analyse the effect of using carbon supported platinum catalysts at the cathode side of a mpDMFC. The effect of the electrode preparation and membrane electrode assembly (MEA) pressing, the effect of the catalyst properties, namely the catalyst loading and metal/support ratio, and the effect of the methanol concentration on the cell performance were studied. The cell behaviour was analysed based on polarisation and electrochemical impedance spectroscopy measurements. Additionally, SEM analyses of some of the electrodes prepared and the commercial ones were also performed to analyse the catalyst characteristics and their impact on the cell performance. The costs associated with each electrode were also analysed, and a cost-to-power trade-off analysis was performed.

It was concluded that the electrode preparation method used is the most suitable one since it leads to similar and, in some conditions, higher performances than the commercial ones. Additionally, better results were achieved with pressing MEAs. Concerning the catalysts, it was possible to conclude that using a supported catalysts has beneficial effects on the system, since it allows a higher platinum dispersion and, therefore, a higher catalyst activity. The results show that, as expected, higher loadings lead to higher performances, but considering the cost-effectiveness of the system, it can be concluded that can be used lower loadings on supported catalysts without a significant loss on the cell performance, reducing these systems cost. It was also verified that the “handmade” electrodes allowed working at high methanol concentrations.

In this work, a maximum power density of $6.9 \text{ mW}\cdot\text{cm}^{-2}$ was achieved using as cathode catalysts $2 \text{ mg}\cdot\text{cm}^{-2} \text{ Pt/C } 60 \%$ and a methanol concentration of 6 M , which is a very interesting result compared to the ones obtained with the most used cathode catalysts in DMFC, $4 \text{ mg}\cdot\text{cm}^{-2} \text{ PtB}$, allowing a significant reduction on the cell costs.

Keywords: methanol, cathode catalysts, carbon supports, catalysts cost, performance

Resumo

Com as metas da neutralidade carbónica em mente, cientistas e engenheiros focam-se em procurar soluções tecnológicas mais sustentáveis. As minicélulas de combustível com alimentação direta e passiva de metanol (mpDMFC) surgem como uma solução sustentável para aplicações portáteis como aparelhos auditivos, telemóveis. No entanto, a comercialização destas células ainda se encontra num estado inicial, devido ao custo associado aos catalisadores utilizados nestas células, catalisadores de platina, e as elevadas cargas usadas.

O principal objetivo desta dissertação foi analisar o efeito da utilização de catalisadores de platina suportados em carbono no cátodo destas células. Estudou-se o efeito da preparação do conjunto membrana eléctrodo (MEA), nomeadamente a preparação e deposição do catalisador na camada de difusão e o efeito da prensagem da MEA, o efeito das propriedades do catalisador, carga e proporção de metal/suporte, e o efeito da concentração de metanol no desempenho da célula. Este foi avaliado com base nos resultados das curvas polarização e ensaios de impedância. Por forma a avaliar as propriedades dos catalisadores e o seu impacto no desempenho da célula, efetuaram-se análises MEV (microscopia eletrónica de varrimento) para alguns dos eléctrodos preparados e os eléctrodos comerciais. Analisou-se o custo associado a cada eléctrodo preparado tendo sido efetuada uma análise da razão custo/potência.

Conclui-se que o método usado para a preparação dos eléctrodos era o adequado uma vez que o seu desempenho foi semelhante e em alguns casos superior ao dos eléctrodos comerciais. Verificou-se também que o desempenho é superior quando a MEA é prensada. No que se refere aos catalisadores foi possível concluir que a adição do catalisador ao suporte tem efeitos benéficos no desempenho da célula, uma vez que permite uma maior dispersão da platina e uma maior atividade do catalisador. Verificou-se também que, de acordo com o esperado, maiores cargas de catalisador originaram melhores desempenhos, mas analisando o custo/benefício destes sistemas, verificou-se que podem ser usados catalisadores suportados com menor carga sem uma perda significativa no desempenho da célula. Os eléctrodos preparados permitiram operar a mpDMFC com concentrações mais elevadas de metanol.

A potência máxima obtida neste trabalho foi $6,9 \text{ mW}\cdot\text{cm}^{-2}$ utilizando $2 \text{ mg}\cdot\text{cm}^{-2} \text{ Pt/C } 60 \%$ como catalisador do cátodo e uma concentração de metanol de 6 M. Este resultado é muito interessante quando comparado com os valores obtidos com o melhor catalisador e carga para estes sistemas, $4 \text{ mg}\cdot\text{cm}^{-2} \text{ PtB}$, permitindo uma redução significativa nos custos da célula.

Palavras-chave: metanol, catalisador do cátodo, suportes de carbono, custo, desempenho

Declaration

I hereby declare, under word of honour, that this work is original and that all non-original contributions is indicated and due reference is given to the author and source

A handwritten signature in purple ink, reading "Deatriz Barbosa Sá Sousa". The signature is written in a cursive, flowing style.

3rd July 2023

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Notation and Glossary

A	Area	m^2
C	Capacitance	F
L	Inductance	H
P	Pressure	Pa
R	Resistance	Ω
R_{act}	Activation resistance	Ω
R_{mt}	Mass transfer resistance	Ω
T	Temperature	K
V_{cell}	Cell potential	V
V_{thermo}	Thermodynamic potential	V
Z_{I}	Imaginary Impedance	Ω
Z_{R}	Real Impedance	Ω

Greek Letters

η_{act}	Activation losses
η_{conc}	Concentration losses
η_{ohmic}	Ohmic losses

List of Acronyms

AFC	Alkaline Fuel cell
CC	Current collectors
CC_MPL	Carbon cloth with a microporous layer
CEFT	Transport Phenomena Research Center
CNT	Carbon Nanotubes
CPE	Constant Phase Element
DAFC	Direct Alcohol Fuel Cell
DL	Diffusion layer
DMFC	Direct Methanol Fuel Cell
EIS	Electrochemical Impedance Spectroscopy
LSRE-LCM	Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials
MCFC	Molten Carbonate Fuel Cell
MEA	Membrane-Electrode Assembly
MOR	Methanol Reduction Reaction
mpDMFC	mini-passive Direct Methanol Fuel Cell
OCV	Open Circuit Voltage
ORR	Oxygen Reduction Reaction
PAFC	Phosphoric Acid Fuel Cell
pDMFC	Passive Direct Methanol Fuel Cell
PEMFC	Proton Exchange Membrane Fuel Cell
SEM	Scanning Electron Microscopy
SOFC	Solid Oxide Fuel Cell

1 Introduction

1.1 Framing and presentation of the work

During the last years, there has been an increase in energy demand, driven by population growth and technological advancements, which has resulted in a growing use of fossil fuels and an intensification of global warming, leading to several climate changes. In 2021, the CO₂ global emissions reached 36.3 gigatonnes, their highest level, from energy combustion and industrial processes [1].

Since 2020 with the pandemic situation and in 2021 with the Ukraine war, the need to find alternatives to fossil fuels to address their scarcity and environmental impact has become more evident and is one of the main goals of scientists, engineers, and politicians. To achieve carbon neutrality by 2050, the focus is on studying and developing new technologies or adapting the existing ones to be more sustainable.

Fuel cells are currently one of the most efficient technologies that convert fuel to electricity and are one of the most promising solutions for transportation and portable applications such as watches, mobile phones, digital cameras, and laptops, replacing lithium batteries and addressing the problems associated with lithium extraction and end-of-life [2]. The most used fuel in these cells is hydrogen. However, the low volumetric energy density of hydrogen and the fact that it is a gas at room temperature make it difficult to handle, storage and use. Direct alcohol fuel cells (DAFCs) emerge as an alternative since the fuels used are in liquid form, making them easier to handle, and have volumetric energy densities considerably higher than hydrogen [3]. In the case of direct methanol fuel cells (DMFCs), the fuel used is methanol that can be green if produced through green hydrogen and carbon dioxide (CO₂) captured from sustainable biomass power plants, promoting the economy related to green hydrogen and the closure of the carbon cycle. These fuel cells have been developed to overcome the fuel storage problem associated with hydrogen and eliminate the need of a reformer to convert methanol into hydrogen.

Passive direct methanol fuel cells (pDMFCs) are a subset of DMFCs that do not require external pumps or controllers to operate, presenting a simpler, lighter, and compact design. However, due to their lower power output, these cells are better suited for low-power devices, such as smartphones, tablets, laptops, photographic cameras, wireless sensors, and medical devices (hearing aids, insulin pumps, continuous glucose monitors, and other implantable medical devices). The required power output is between 3 W and 50 W, for cameras and mobile phones and laptops, respectively [3-5]. Passive DMFCs can be a reliable power source for outdoor and recreational activities such as camping, hiking, and boating. They can power GPS

devices, radios, lights, wireless sensors and monitoring systems in remote locations, where access to the electricity grid is limited [6-8].

However, there are still some technical problems that prevent the commercialisation of the pDMFCs on a large scale, such as the slow kinetics of the electrochemical reactions and the methanol crossover phenomenon [9]. Another limiting factor of these systems is the high cost of the catalysts used, since the most widely used catalyst is platinum, which is a rare, noble, and expensive metal [6]. So, the development of low-cost and improved catalysts, to reduce these systems costs without a significant loss of efficiency, is mandatory.

The main objective of this work is to study the influence of using platinum-supported carbon catalysts in the cathode side of a passive DMFC, evaluating their impact on cell performance as well as cost-effectiveness, considering the use of this technology for portable applications, where the energy demand is lower. Parameters such as pressing the membrane electrode assembly (MEA), the cathode catalyst loading and the metal (Platinum) mass fraction, and the methanol concentration were evaluated. The performance of the laboratory-prepared catalysts was also compared with the commercial catalysts.

1.2 Contribution of the author to the work

The experimental work was divided between the Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM) and the Transport Phenomena Research Centre (CEFT). The electrodes were prepared by the airbrush method at LSRE-LCM, the MEA pressing was also performed at LSRE-LCM and the cells assembling was performed at CEFT. The polarisation and EIS measurements were performed at CEFT in order to assess and quantify the performance of the cell in the different configurations studied.

1.3 Organisation of the dissertation

This dissertation is divided into six chapters. The first refers to an introduction and framing of the work, followed by a chapter where the theoretical fundamentals are presented. In this second chapter, an analysis of the background and technology of fuel cells is made, moving on to an overview of the passive and direct methanol fuel cell technology. Chapter 3 refers to the experimental work carried out during the dissertation and presents the materials and methods used. All the protocols used were presented, as well as the structure of the cell and the equipment's used and all the tests carried out. Chapter 4 focuses on the presentation and discussion of the main results obtained. Chapter 5 presents the final conclusions, and chapter 6 presents an assessment of the work carried out.

2 Context and State of the art

2.1 Background

The development of fuel cells become urgency due to the imminent threat of energy scarcity caused by the depletion of fossil fuels. Moreover, the number of emissions due to the unregulated combustion of these fuels is one of the major concerns for environmental pollution. Fuel cells are considered emission-free devices, making them a favourable option in pursuing sustainable and emission-free energy technologies [9].

Looking at the technology behind the fuel cells, their principal goal is to produce electricity, converting the chemical energy present in the fuel into electrical energy. As long as the fuel and the oxidant are supplied to the cell, they can produce electricity without the need to be recharged or store energy, like batteries. As the conversion of chemical energy into electrical energy, in fuel cells, does not require the conversion into mechanical or thermal energy as in traditional engines, the thermodynamic limitations, as seen in Carnot cycle, do not exist [3]. Based on that, fuel cells are known as effective electrochemical converters and have been used in different applications, including transportation, stationary power generation, portable devices, and emergency backup power applications, and are expected to be a major driver of distributed power, allowing homes and businesses to generate/produce their energy efficiently [8, 10-13]. Although fuel cells differ from batteries, which are designed for continuous replacement of the reactants consumed, their basic working principle is the same. It consists of two electrodes (anode and cathode) separated by an electrolyte which separates the electrodes and drives the ions [10, 14, 15]. The choice of electrolyte and fuel, which consecutively determine the electrode reactions and the type of ions that carry the current across the electrolyte, leads to different types of fuel cells (Figure 2.1) [8, 13, 14].

The electrochemical principle is the same for all fuel cell types; however, as can be seen in Figure 2.1 the operating principle and temperature are different, leading to different efficiencies and allowing its use for different energy demands [16]. The properties of the materials used in each fuel cell type are determined by the operating temperature and the cell lifetime.

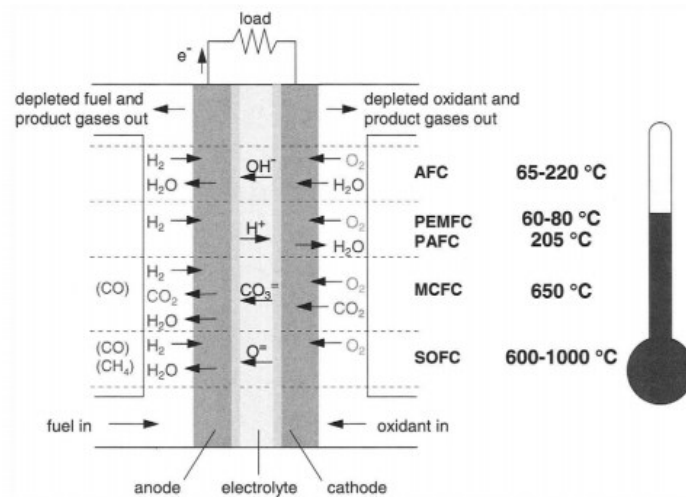


Figure 2.1 - Scheme of the different fuel cell types [17]. AFC: Alkaline Fuel Cell; PEMFC: Proton Exchange Membrane Fuel Cell; PAFC: Phosphoric Acid Fuel Cell; MCFC: Molten Carbonate Fuel Cell; SOFC: Solid Oxide Fuel Cell.

Most fuel cells under development use gaseous hydrogen, or a synthesis gas rich in hydrogen, as a fuel. Hydrogen has a high reactivity for anode reactions and can be produced chemically from a wide range of fossil and renewable fuels, as well as via electrolysis. For similar practical reasons, the most common oxidant is gaseous oxygen, which is available in air.

By examining the emissions by the subproducts and products released from fuel cells, it is possible to conclude that the emissions of regulated pollutants like carbon monoxide, nitrous oxides, sulphur oxides, and particles are significantly lower than current air quality regulations and are usually negligible. Furthermore, even carbon dioxide emissions are reduced with a fuel cell system due to a higher system efficiency and lower fuel consumption [2, 12, 18].

One major drawback of fuel cells is that they typically rely on expensive noble metals as catalysts to achieve high efficiencies, which significantly increases their costs. For fuel cells that use hydrogen, the purity of the fuel must be carefully maintained to avoid catalyst poisoning, leading to additional costs for fuel transport and storage [11].

Engineers and scientists are actively searching for different materials and manufacturing techniques to improve the fuel cell efficiency, durability, and reliability, and enhance the fuel cell design to decrease the cell costs. These advancements will enable fuel cells to compete with the existing technologies: combustion engines and batteries [12].

2.2 Passive Direct Methanol Fuel Cells

2.2.1 Fundamentals

Hydrogen and liquid alcohols, such as methanol, ethanol, 1-propanol, 2-propanol, or ethylene glycol, are the fuel choices in PEMFCs for portable application. Looking at the

advantages of using alcohol as fuel, it is important to emphasize that it is liquid at room temperature and can be transported and stored in tanks, canisters, or barrels. Among the different alcohol used, methanol is the best one for portable applications since as the highest energy-to-carbon ratio than any other alcohol [19]. Moreover, methanol has a high energy density, around $6.1 \text{ kWh}\cdot\text{kg}^{-1}$ and a low freezing point of -97°C , being suitable for use in cold ambient temperatures [20]. Due to its versatility, methanol is traded globally and in Europe, the net price for methanol is around 0.50 € per liter [21]. Methanol is toxic, so it is necessary to be careful handling, and must be very pure because the DMFCs are very sensitive to the impurities present in the fuel [3, 9, 21]. However, DMFCs normally use very diluted methanol solutions, so the toxicity of methanol is not a major issue.

DMFCs are considered a particular type of PEMFCs, as they have the same operating principle, temperature range and structure, including the solid electrolyte membrane used as electrolyte, and have been developed to overcome the hydrogen distribution and storage problem and to eliminate the need for a reformer to convert methanol into hydrogen. Additionally, they have a fast start-up time and do not have components that make noise or vibrations [6, 21]. A conventional combustion-based power plant generates electricity at efficiencies of 33 % to 35 %, while direct methanol fuel cells can generate electricity at efficiencies up to 60 % and even higher with co-generation [22].

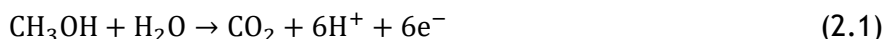
There are different modes of operation of the DMFCs based on the reactants supply: active, passive, or semi-passive. Active DMFCs use pumps or compressors to supply fuel and oxidant to the anode and cathode, respectively. These systems have a better performance, and it is possible to control their operating temperature; however, they have moving parts, a more complex design, which is not suitable for portable applications, and require an external input of energy or the electrical energy produced by the system to power the external devices used to supply the reactants, which reduces their efficiency and increase its costs [3, 9]. On the other hand, passive DMFCs (pDMFCs) operate exclusively through natural phenomena such as diffusion, convection, and evaporation. In this way, the methanol is placed in a reservoir presented at the anode, and the oxidant (oxygen from the air) reaches the cathode through natural convection since the cathode is open to the air. These systems do not have additional components, are more compact and lighter, work at room temperature and pressure, do not require energy input and have lower costs [19, 23]. This allows them to be very suitable for portable and low-power applications. As pDMFCs have a longer shelf life compared to batteries, they are ideal for emergency situations where immediate power is required [6]. In semi-passive systems, one side is actively fed, while the other is fed passively. Thus, only one side requires additional components and an input of energy. These systems have the advantages and

disadvantages of both feeding modes, active and passive, and are usually used for intermediate power requirements and when the system size and weight is not an issue [3, 19].

Recent lab-scale developments suggest that the massive use of DMFCs may become a reality, especially with the development of mini passive direct methanol fuel cells (mpDMFCs) that can be seamlessly integrated into small electronic devices [24].

2.2.2 Basic principle of operation

Focusing on the theoretical principle of operation, the main goal of a DMFC is to convert the chemical energy of methanol into electrical energy. The methanol (CH_3OH) is electrooxidized in the anode compartment, producing carbon dioxide (CO_2), protons, and electrons in the presence of water (H_2O) under acidic conditions (Equation (2.1)). The protons move to the cathode compartment through the membrane while the electrons flow through the external circuit to the cathode, generating the electric output of the cell. At the cathode, oxygen reacts with protons and electrons, producing water (Equation (2.2)). The overall reaction is presented in Equation (2.3) [9, 20].



Although they are not emission-free, as can be seen in Equation (2.1), the DMFCs can be considered environmentally friendly because they do not release toxic by-products and, if formed (aldehydes, ketones, and carboxylic acids) have very low concentrations and the CO_2 (a greenhouse gas) emissions are very low having no impact on the environment [3].

Perfluorinated polymer membrane, known as Nafion®, is the most used membrane in the DMFCs due to their high chemical stability, mechanical strength, thermal stability, and excellent proton conductivity. Nafion® 112, Nafion® 115 and Nafion® 117 are some of the commercially available Nafion® membranes used in pDMFCs that only differ in their thickness [19, 25].

The electrocatalytic oxidation of methanol is a multistep reaction that results in the formation of intermediate species, such as CO. The adsorption of CO on the catalyst active sites leads to a sluggish kinetic and a loss of efficiency. So, a good catalyst for the methanol oxidation reaction (MOR) should provide high catalytic activity, porosity, electrical conductivity, and active surface area, with a significantly lower affinity to CO.

Therefore, binary Pt-based alloys, such as Pt-Ru, Pt-Os, Pt-Sn, Pt-W, Pt-Mo have been studied to improve the methanol oxidation activity [9, 23, 26]. Pt-Ru emerged as the most

effective binary catalyst, with ruthenium (Ru) serving as adsorption sites to form OH_{ads} that react with CO to generate CO_2 and protons, allowing complete methanol oxidation [19, 26, 27]. It is commonly accepted by the scientific community that the ideal Pt-Ru ratio is 1:1 and to achieve satisfactory fuel cell performances, considering the fuel cell's lifespan, it is necessary a high catalyst loading (around $2\text{--}8 \text{ mg}\cdot\text{cm}^{-2}$) [26, 28, 29].

At the other electrode of a DMFC, the catalyst choice is determined by its catalytic activity for the oxygen reduction reaction (ORR), which follows a two-electron transfer pathway producing hydrogen peroxide and a four-electron transfer pathway, producing water. The most used cathode catalyst is Pt, which despite its high cost, is highly active to the ORR [23].

2.2.3 Performance losses

The theoretical overall cell voltage of a DMFC can be calculated considering the potential of the reduction and oxidation reactions that occur in these cells. Thus, the DMFCs have a theoretical overall cell voltage of 1.21 V at 25°C and 1 atm. In practice, this value is much lower, due to four irreversible losses that affect these systems: activation, ohmic, mass transport and crossover losses (Figure 2.2) [30, 31].

So, the real cell voltage can be estimated by subtracting all the overvoltage losses from the thermodynamically predicted voltage:

$$V_{\text{cell}} = V_{\text{Thermo}} - \eta_{\text{act}} - \eta_{\text{conc}} - \eta_{\text{ohmic}} \quad (2.4)$$

In Equation (2.4), V_{Thermo} is the thermodynamically predicted voltage of the fuel cell, η_{act} is the activation losses due to the slow reaction kinetics, η_{ohmic} is the ohmic losses from the ionic and electronic resistances and η_{conc} is the concentration losses due to mass transport [9].

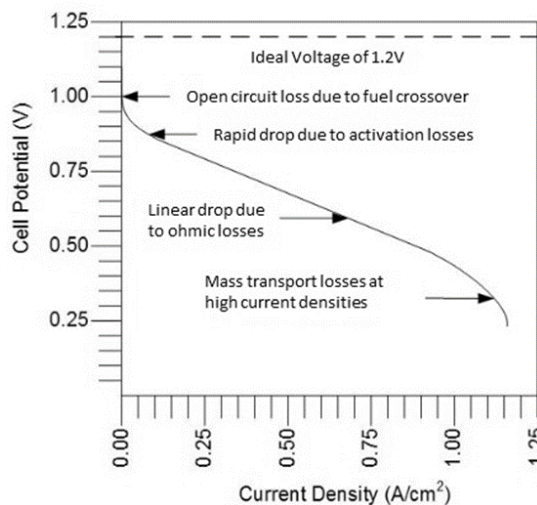


Figure 2.2-Typical polarisation curve of a DMFC [31].

The crossover losses are more relevant at the open circuit voltage (OCV) (where no current is applied to the cell) resulting in a significant drop in the OCV, being the first loss that negatively affects these systems. These losses occur due to the methanol concentration gradient between the anode and the cathode side, based on the Fick's law of diffusion, the methanol trends to spread from a higher concentration region to a lower one, and since the membrane is not impermeable to methanol. Consequently, the methanol crosses the membrane into the cathode compartment lowering the cell power output due to the generation of a mixed potential at the cathode side. This is due to the occurrence of the undesired MOR at the cathode, which poisons the cathode catalyst and decreases the catalyst active sites for the ORR. Moreover, this led to a loss of fuel at the anode side that could be used on the MOR to produce energy. [30]

The activation losses occur at low current densities due to the activation energy needed for the electrochemical reactions to occurs in the catalysts [3, 32]. As can be seen in Equation (2.1), one methanol molecule releases six protons and six electrons during its complete oxidation to CO_2 . However, a complete methanol oxidation is difficult to achieve, and often partial electron transfer occurs, leading to the formation of intermediates that are detrimental to the cell efficiency [33].

The ohmic losses are the main losses that occur at intermediate currents and are a consequence of the charge transport resistances (ions and electrons) in the external circuit and membrane. However, the ions transport has a more relevant impact on these losses. In this region, the cell potential decreases linearly with the current following Ohm's law.

At high current densities, the dominant loss is the mass loss that is due to the reactants and products transport limitations, due to the occurrence of a two-phase flow phenomena since the anode reaction product, CO_2 , is a gas and the anode is liquid, and the cathode reaction product is liquid water, and the cathode is gaseous. Additionally, if these products are not properly removed from the cell, they will block the reactant access to the reaction zone, catalyst layers [2, 6, 31].

2.2.4 Performance evaluation and diagnostics

The most common way to evaluate the performance of a DMFC is by a polarisation curve, where is plotted the cell potential versus the current density (Figure 2.2). By using this method, it becomes possible to identify the key factors that contribute to the cell performance loss, including activation losses, ohmic losses, concentration losses, and crossover losses. Nevertheless, quantifying and correlating these losses with the various processes and parameters that affect the DMFCs technology can be a challenging task. Additionally, each type of loss depends on the fuel cell operating conditions and configuration, such as materials, design and construction [32].

In order to better understand the relationship between the cell behaviour and the properties and structure of each component, various diagnostic tools such as electrochemical impedance spectroscopy (EIS) have been employed in fuel cell systems diagnosis [32]. EIS, a well-established and non-invasive diagnostic technique, has been extensively used due to its accuracy and versatility, enabling the analysis and quantification of the effect of a broad range of phenomena and characteristics of the fuel cell on its performance [32].

In the EIS technique a sinusoidal perturbation is applied to the system, and the response is measured over a wide range of frequencies. Impedance measurements in DMFCs are usually performed in a potentiostatic mode (setting the cell potential and measuring the current) and generally use an amplitude range between 5 to 15 mV and a frequency range from 1 mHz to 100 kHz with 10 points/decade [25, 32, 34]. The EIS results are displayed as an impedance spectrum, which can be represented by a Nyquist or Bode plot. The Nyquist plot is the most widely used, where the imaginary component of the impedance is plotted versus the real one (Figure 2.3). On the other hand, the Bode plot displays the amplitude or phase of the impedance as a function of frequency. Both representations allow identifying the different losses that negatively affect cell performance.

Figure 2.3 present a typical Nyquist plot of a DMFC with the three major losses that affect the system under operation, when current is applied to the cell: activation, ohmic and mass transfer losses.

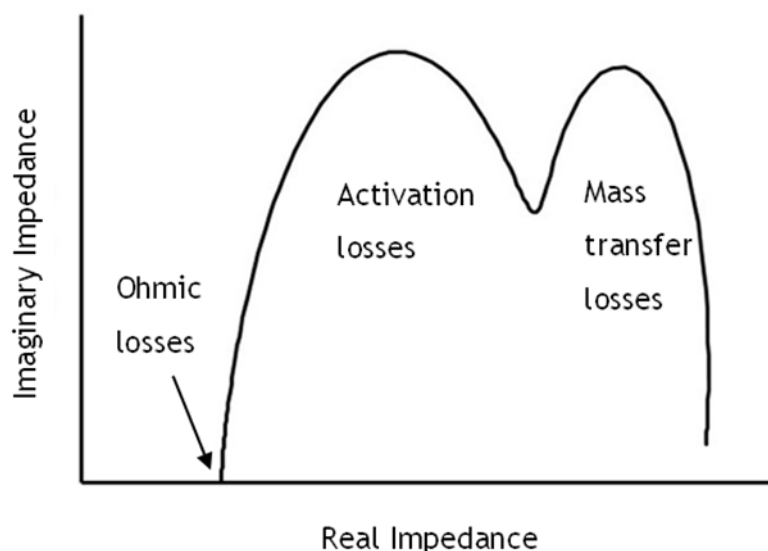


Figure 2.3 - Representation of a typical Nyquist plot with the three major losses. Adapted from [3].

The real impedance axis and the imaginary impedance axis intersect at the high-frequency region, indicating the ohmic losses and the ohmic resistance, which includes contact, ionic, and electronic resistance. In the medium-frequency region, the Nyquist plot exhibits an

arc that corresponds to the activation losses and/or charge-transfer resistances. This arc decreases as the voltage decreases and results from the MOR at the anode and ORR at the cathode. At the low-frequency region, the arc indicates the mass transfer losses and is characterised by an increase of the resistance with a decrease of the fuel cell voltage [9, 15, 32].

The EIS results can be analysed by fitting the impedance spectrum with an equivalent electric circuit, as the one shown in Figure 2.4, to quantify the different losses that affect the system under study. Depending on the characteristic and shape of each spectrum, different electric elements, such as resistors, capacitors and inductors, and combinations between them must be considered.

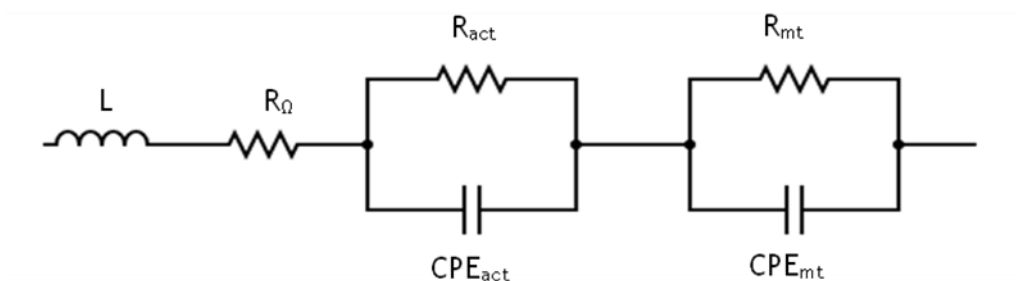


Figure 2.4 - Schematic representation of an EEC.

The resistor (R) is used to represent the electrical resistance that is time-independent, following the Ohm's law. Due to its frequency independence, the resistor only has a real part, represented in the Nyquist plot by a single point at the real axis, representing the ohmic losses, R_Ω , (Figure 2.3 and 2.4). The inductance (L), on the other hand, only has an imaginary part. In these systems, the inductive behaviour is due to the adsorption of different species at the catalyst surface. In fuel cells, the capacitor is normally replaced by a constant phase element (CPE) since the current is not uniformly distributed and the reaction rates on the electrode surface are not homogeneous.

Analysing Figure 2.3, it is possible to see two arcs, which represent the activation and mass transfer losses, that can only be described using two parallel combinations of a R and a CPE [32]. Therefore, besides the Resistor that described the ohmic losses and the system inductive behaviour the EEC that describes the plot presented in Figure 2.3, must have two parallel R -CPE elements to represent the activation and mass transport losses, R_{act} - CPE_{act} and R_{mt} - CPE_{mt} , respectively.

However, when conducting the EIS measurements on a pDMFC, activation and mass transfer resistances occur simultaneously on both sides (anode and cathode), leading to an overlap of the two arcs, making difficult to distinguish the activation and mass transfer losses of each electrode.

The main challenge is to establish a link between the activation and mass transfer losses and the various phenomena and processes that characterise an operating pDMFC. Additionally, the methanol that crosses the membrane from the anode to the cathode side, reacts at the cathode side, which could lead to an additional resistance [32, 34].

Moreover, in some conditions, the mass transport region is not reached, and therefore none of the resistances that negatively affect the fuel cell performance are due to the mass transfer losses. As a result, the Nyquist plot shows an arc at the low-frequency region, which is not related to mass transport losses but to activation losses [34].

2.2.5 Challenges and Prospects

For a long time, researchers and engineers have anticipated that the DMFC technology will revolutionise the electronics field, particularly by replacing conventional batteries and powering portable and handheld devices.

The United States Department of Energy (DOE) has selected 28 hydrogen and fuel cell R&D projects, which also include DMFC, as an initiative to produce and use hydrogen across multiple energy sectors. As a result, government initiatives and private sector investments are expected to drive the development of this technology towards its introduction in the market [22, 35]. There are also some recent investments of companies in this sense, such as Weltmeister, a Chinese car brand, which is developing a fuel cell car using a DMFC [36].

In January 2021, Johnson Matthey won a new multi-million-pound agreement to provide 400 000 direct methanol fuel cell components to SFC Energy AG, a global leader of hydrogen and direct methanol fuel cells for stationary and mobile hybrid power solutions. The agreement started in February 2021 and as a duration of three years [22].

However, the chemical-to-electrical energy conversion efficiencies in DMFCs are still lower and its costs are higher than the traditional power sources available in the market, requiring additional research and development efforts to overcome that. This is due to the high methanol crossover rates through the membrane, high cost and limited availability of the noble metals used as catalysts, namely Pt and Ru and poisoning of the cathode catalyst by the adsorbed intermediates species generated in the MOR that occurs at this side, leading to sluggish reaction kinetics [9, 26].

For commercialisation and massive use of this technology, it is vital to develop a low-cost anode and cathode catalyst with high activity and a low-cost membrane with a reduced methanol permeability.

The combination of fluorinated and non-fluorinated materials in composite membranes offers several advantages over traditional fluorinated membranes like Nafion®, including lower costs and methanol crossover rate and higher ionic conductivity. However, these hybrid

membranes still have lower performances than the Nafion® membranes. Despite the ongoing efforts to develop new membrane materials, Nafion® membranes remain the most used ones as they still lead to higher performances [4]. Further research is needed to develop hybrid membranes that can deliver high performance and affordability. Thicker membranes such as Nafion® 115 and Nafion® 117 are preferred as they present lower methanol crossover rates and therefore, improved performances [9].

As mentioned, Pt-Ru catalysts with higher loadings have been the most used at the anode side of a DMFC [23, 37]. To mitigate these catalyst costs, a lot of research has been carried out to study the MOR and the anode catalyst activity towards reducing the catalyst loading and improving the catalyst activity and utilization [26, 28, 29]. This can be achieved by exploring alternative non-noble catalysts and/or implementing supporting strategies to enhance the catalyst activity [29, 38, 39]. Various transition metal oxides, such as titanium oxide and manganese oxide, were also used as the anode catalyst for high activity towards the MOR. Moreover, very few noble metals (Pd, Ru, OS, etc.) with a base metal (Fe, Co, Ni, etc.) have been used for methanol electrooxidation. The catalyst Pd-Ni with a high palladium ratio gave the highest activity [40, 41]. Based on these efforts, it was verified that Pt-free materials have a good potential to resist to CO poisoning, but very low performances.

In the cathode, the most used catalyst is platinum black, which is a rare, noble, and expensive metal [18]. The development of low-cost and improved catalysts for the cathode side is another prospect to reduce these systems costs. One approach to reach a catalyst with higher activity involves dispersing the active phase, metal, on a support material with excellent conductivity. This method allows a reduction in the amount of metal used and an improvement in the electrical conductivity and porosity due to a higher surface area [33].

Carbon black has been widely used as a support material for catalysts being Vulcan XC- 72 the most used one, due to its low cost, and high activity and conductivity, so they can act as a path for the electrons flow [42]. Additionally, other carbonaceous materials such as graphene, carbon nanotubes, mesoporous carbon nitride materials, or carbon nanofibers can be used [43]. Alternatively, non-carbonaceous materials like silica, titanium dioxide, or aluminium oxide can also be used as suitable support materials [6, 33, 43].

Different studies revealed that the physical properties of the carbon supports could positively affect the electrochemical properties of the catalyst. It has been reported that carbon materials with a high surface area and crystallinity can provide a higher dispersion of the Pt nanoparticles and consequently enable electron transfer, resulting in a better cell performance. However, a high specific surface area is associated with small pore sizes, which could not be advantageous to the reactants and products mass transport. Therefore, it is

necessary to achieve an optimized carbon structure to reach the highest catalyst performance [33, 44].

Pt and Pt-based alloy catalysts are impregnated on the carbon support material by different chemical synthesis methods, such as impregnation-reduction, colloidal methods, etc. These chemical methods are suitable for the mass production of Pt catalysts; however, improvements in dispersion and size distribution are still required to achieve high mass activity [6, 45].

As mentioned, one of the major drawbacks of the DMFCs is the methanol that crosses the membrane towards the cathode side, reacting on the cathode catalysts. Therefore, the cathode catalysts should have a high tolerance to the presence of methanol, and Pt is not the best one to that. Some complex metals, such as Fe and Co porphyrins or phthalocyanines, and transition metal oxides, non-noble cathode catalysts, have been tested as DMFC cathode catalysts and have shown remarkable selectivity to ORR and inertness to methanol oxidation [29, 46, 47]. Unfortunately, most transition metal oxides have been found to be unstable in the acidic environment of cell operation [48].

As single component catalysts that have shown improvements for the ORR is important to highlight catalysts such as Au, Ag, Pd, nitrogen (N)-doped graphitic carbon, N-based carbon nitride and N-doped carbon nanotubes (CNTs). Additionally, carbon materials have been identified as some of the most promising materials for DMFCs in acidic media due to their high chemical stability and high electric conductivity [26, 47, 49].

Pt-Fe, Pt-Au, Pt-Co, Pt-Bi, Pd-W and Pt-Cu are examples of bimetallic electrocatalysts studied for the cathode of DMFCs, the Pt-Au being the most promising. However, when using transition metals is important to consider the dissolution of both transition metals in acidic media, limiting their application in DMFC [49-53].

Multiple-component cathode catalysts, such as Pt/CoSe₂, exhibited a high ORR activity in acidic media and are considered a methanol-tolerant catalyst, which could reduce the costs and improve the ORR activity when compared to pure Pt catalysts [48, 49].

The design and performance optimisation of the cathode electrode should be enhanced to increase the DMFCs performance. A key aspect is to use thinner electrodes to allow a proper proton conductivity and oxygen diffusivity [54]. Conventional methods for electrodes preparation involve the use of catalyst inks, applied onto the membrane or on a carbon-based diffusion layer, by pasting, brushing, or spraying. These techniques tend to introduce irregularities when working with large electrode areas and are performed manually. These aspects have an impact on the electrode overall structure and catalyst composition, affecting the mass transport and kinetic properties of the electrode [54, 55].

The traditional ink preparation involves mixing the catalyst, isopropanol, and a Nafion® ionomer solution, which acts as binding. However, Birry et al. [55] fabricated an improved electrode using an additional solvent, n-butyl acetate, to control the polarity of the cathode catalyst ink. This addition resulted in an increase in the electrochemical active surface of the cathode catalysts to the ORR, and a decrease in the methanol crossover effect, due to the formation of small catalyst-Nafion® ionomer agglomerates and organized networks of Nafion® ionomers.

Despite all the work done to replace the anode and cathode catalysts used in a DMFC, there are still some obstacles to overcome to achieve the cost-effectiveness needed for these systems. It is crucial to optimise the synthesis methods, shape, metals and supports selection and structure, with single, double, or multiple components, to overcome the physical and chemical limitations that compromise the DMFCs performance [49].

Another problem of these systems is their performance degradation over time, which can be reversible or irreversible [14]. Reversible degradations are generally associated with the accumulation of CO₂ in the anode and water flooding at the cathode. Irreversible degradation is caused by irreversible changes related to the materials or MEA configuration, such as agglomeration of catalytic particles, deactivation of active catalyst sites because of adsorption of reaction intermediates and fuel impurities, oxidation of the catalyst support, membrane degradation, and changes in the hydrophobic properties of the diffusion layers [14, 19, 56]. Even though degradation is inevitable, it can be minimized through an understanding of the degradation and failure mechanisms, which can be achieved by the development and application of different diagnostic techniques, such as polarization and EIS measurements.

Despite the several problems, DMFCs are still an interesting technology to replace fossil fuel-based technologies, and the focus remains on addressing these barriers to optimise these cell systems, whether in cost, performance, or a cost-performance ratio. Thus, researchers worldwide are actively involved in the R&D aspects of DMFC as well as mini-DMFC to make this technology economically and commercially viable to achieve a cleaner and safer environment [34].

3 Materials and Methods

In the experimental work, the tests were all performed using a mini passive DMFC (mpDMFC). This chapter describes all the procedures undertaken, as well as the components and configuration of the fuel cell studied, and the test equipment used to evaluate the performance of the mpDMFC.

3.1 Fuel cell design

The cell used during the experimental work is a mini passive DMFC since it has an active area of 2.25 cm^2 . The cell as a total area of 16 cm^2 and is composed by: end plate, current collector, diffusion and catalyst layer at the anode, membrane and end plate, current collector, diffusion and catalyst layer at the cathode (Figure 3.1). All the different components of the cell will be described in this section.



Figure 3.1 - mpDMFC used in the experimental work (front and lateral view, respectively)

Looking at the more external part of the cell, the end plates are used to support the cell and to close it. These plates are shown in Figure 3.2 and are made of acrylic, as it provides the necessary stiffness and transparency for viewing the cell's interior, with dimensions of $4 \times 4 \text{ cm}$. The cathode plate has a thickness of 0.5 cm and has a hole in the middle with an area of 2.25 cm^2 (active area of the cell) for the oxygen supply. The anode plate has a thickness of 1 cm , as it has a reservoir with 1.8 cm^3 ($0.8 \times 1.5 \times 1.5 \text{ cm}$) where the methanol solution is placed.

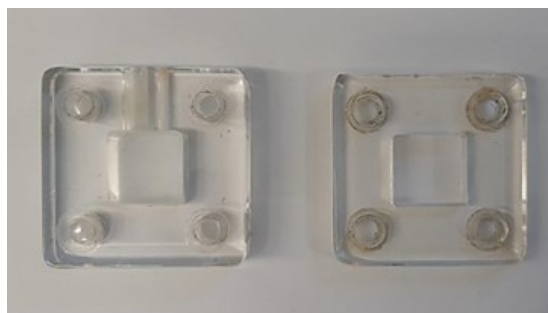


Figure 3.2 - Anode (at left) and cathode (at right) end plates of the mpDMFC.

Rubber insulating plates are used between the end plate and the current collector to prevent current leakage and short circuits and the electric contact between these layers (Figure 3.3).

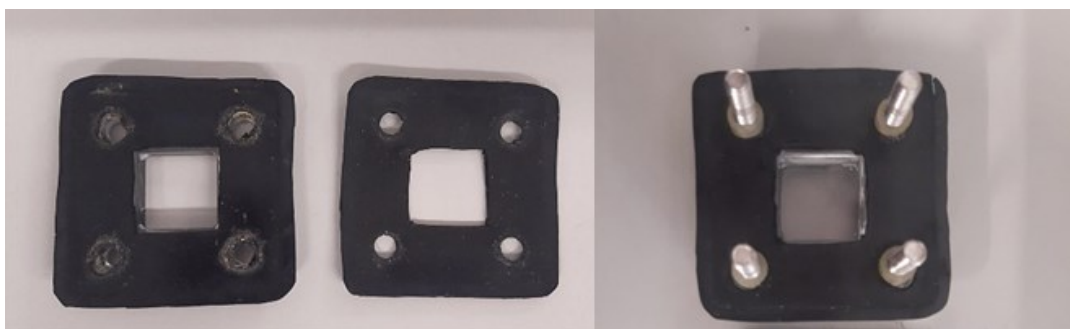


Figure 3.3 - Rubber insulating plates.

To collect the electrons produced at the anode and transfer them to the cathode and enable the reactants supply and products removal, the current collectors (CC) used are made of stainless steel 316L and have a thickness of 0.2 cm. This material is used since it has a high electrical conductivity, mechanical and corrosion resistance, and is cost-effective [57]. Figure 3.4 shows the current collectors used at the cathode (left) and anode (right). The anode current collector has 81 round holes with a diameter of 1 mm and a spacing of 0.5 mm between them, leading to an open ratio of 28 %. The cathode current collector has 49 holes with a diameter and a spacing of 1 mm and an open ratio of 17 %. These plates may have different shapes and opening ratios that will have an impact on the cell. Therefore, the characteristics of the CC used in this work were chosen based on previous research team results that showed that these designs lead to better performances.

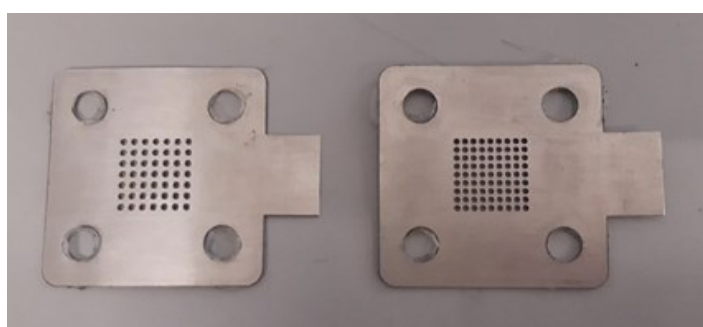


Figure 3.4 - Anode (at left) and cathode (at right) current collectors of the mpDMFC.

In the middle of the cell is the MEA (membrane electrode assembly), consists of a proton exchange membrane between an anode and cathode electrode (Figure 3.5).

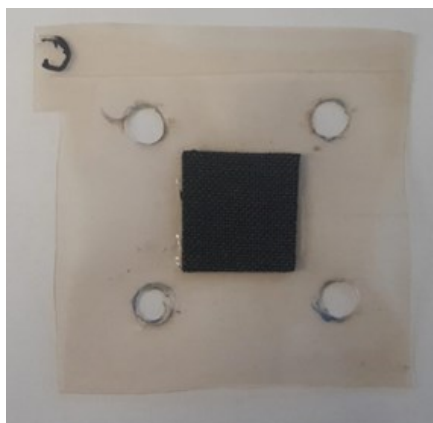


Figure 3.5 - Example of a MEA used in the experimental tests.

The electrodes are supported on macroporous carbon paper or carbon cloth called as diffusion layer (DL), which allows the reactants and products reactants and products, coated with a catalyst layer, where the reactions take place where the reactions take. Each electrode consists of a diffusion layer that is coated with a catalytic layer. The electrodes are placed at the centre of the membrane, and they have an active area of 2.25 cm^2 ($1.5 \times 1.5 \text{ cm}$). To ensure that electrodes are well attached to the membrane the MEA can pass through a hot-pressing process [58]. The effect of this procedure on the cell behaviour was evaluated in the present work.

In all the tests, the membrane used was Nafion® 117, pre-treated at the laboratory and explained in section 3.3.1, and the cathode diffusion layer was made of carbon cloth with a microporous layer (CC_MPL), having a porosity of 0.80 and a thickness of 0.410 mm. The anode electrode was made of carbon cloth with a microporous layer (CC_MPL) coated with a catalytic layer of $3 \text{ mg} \cdot \text{cm}^{-2}$ Pt-Ru. All the components were supplied by Fuel Cells Etc.

Towards a cost reduction, the catalytic layer was a topic of study and was evaluated by the use of platinum supported carbon (Vulcan XC-72) catalysts with different metal/support ratios and metal loadings (Table 3.1).

The cathode electrodes were prepared in LSRE-LCM, and the method used for depositing the catalytic layer on the diffusion layer will be explained in this chapter. As the electrodes were handmade, the loads obtained were very near the desire ones, as shown in Appendix A.2, Table A.2.1. In some conditions, the handmade electrodes were compared with the commercial ones, supplied by Fuel Cell Store, to validate the techniques used to prepare the handmade electrodes.

Table 3.1 - Studies performed with the mpDMFC.

Experiment	MEA	Cathode Electrode
1	Not pressed	$0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60% commercial
2	Pressed	$0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60% commercial
3	Not pressed	$0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60%
4	Pressed	$0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60%
5		$4 \text{ mg}\cdot\text{cm}^{-2}$ PtB
6		$4 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60%
7		$4 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 40%
8		$2 \text{ mg}\cdot\text{cm}^{-2}$ PtB
9		$2 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60%
10		$4 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 40%

When all the components of the cell are put together, nuts and bolts are required to assemble the mpDMFC. To ensure that the same force is applied to the four bolts, it was used a torque key, using a torque force of 3 N.m. on each bolt. This procedure promotes a uniform pressure and avoids the occurrence of leaks.

3.2 Test station

To perform the polarisation and impedance measurements, an electrochemical station, provided by Zahner Elektrik GmbH & Co. KG, was used. This station was connected to the mpDMFC anode and cathode current collector plates by two wires and to the Thales USB software that is used for data acquisition and reading (Figure 3.6).

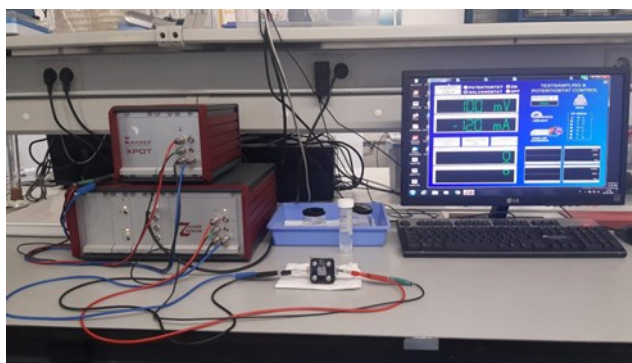


Figure 3.6 - Experimental Setup

3.3 Procedures

3.3.1 Membrane preparation

As mentioned before the Nafion® 117 membranes were pre-treated at the LSRE-LCM. The procedure adopted was the one already used by the research team:

1. Hydrate the membrane in distilled water for 10 min.
2. Immerse the membrane in a 3 % (V/V) hydrogen peroxide (H_2O_2) solution at 80 °C for 30 min.
3. Wash the membrane with distilled water.
4. Immerse the membrane in a solution of distilled water at 80 °C for 30 min.
5. Immerse the membrane in a 0.5 M sulfuric acid (H_2SO_4) solution at 80 °C for 30 min.
6. Wash the membrane with distilled water.
7. Finally, store the membrane with distilled water.

The experimental setup is shown in Appendix A.1, Figure A.1. as well as the explanation of the calculations performed to prepare the H_2O_2 and H_2SO_4 solutions.

3.3.2 Electrode preparation

For the electrode preparation, consisting of the deposition of the catalytic layer in the diffusion layer it was employed the airbrush method, since as already concluded by the research team, this is the more accurate method. The ink preparation involved mixing the catalyst, (supplied by Fuel Cell Store in the form of dust), isopropanol and 5 % wt.% of a Nafion® ionomer solution.

The experimental procedure adopted was the following:

1. Weight the diffusion layer with the electrode dimensions (1.5 x 1.5 cm).
2. Weigh a certain mass of catalyst to obtain the desired metal load.
3. Mix the previously weighed catalyst with a given 5 % Nafion® solution. Then, add an isopropyl alcohol solution to the mixture of catalyst and Nafion® solution.
4. Place the prepared ink in an ultrasonic bath for 30 min, so that it disperses.
5. Finally, deposit the paint on the diffusion layer using an airbrush and over a hot plate at 40 °C, to evaporate the propanol.
6. Leave for 30 min at room temperature to dry, and then reweigh the diffusion layer with the catalyst to obtain the catalyst load.

If the desired load is not obtained in the first deposition, the calculations are adapted for the missing charge and then follow the same procedure. The airbrush used to make the deposition as well as the experimental setup can be seen in Appendix A.2, Figure A.2 and A.3, respectively. The Airbrush brand's is Infinity CRplus. The catalyst mass, the volume of the 5 %

Nafion® solution and isopropanol used for the different electrodes studied are summarised in Appendix A.2, Table A.1.

3.3.3 MEA pressing

The effect of pressing or not the MEA on the cell performance was tested in order to decide the best procedure. The experimental setup for the MEA can be found in Appendix A.3, Figure A.5, and the procedure adopted was:

1. Turn on the bath attached to the press.
2. Turn on the press and set a temperature of 130 °C and let it stabilise.
3. Place the MEA in the press and let it stabilise for 5 min.
4. Press for 90 sec at 2.5 ton ($35 \text{ kg} \cdot \text{cm}^{-2}$).

In order to help the process, Teflon® in an envelope-shaped (Appendix A.3, Figure A.4) was used to support the MEA and prevent the electrodes from not being properly aligned in the centre of the membrane.

3.3.4 Polarisation and EIS measurements

The procedure adopted to perform these measurements are in accordance with the ones used by the research group in previous optimization studies with passive and mini passive direct methanol fuel cells.

Before performing the first polarisation measurement for each condition tested, the mpDMFC was activated with a methanol solution of 3 M and at the open circuit conditions until the OCV remained constant. The preparation of the methanol solutions can be found in Appendix A.4. The polarisation measurements procedure was:

1. Filled the anode reservoir with the methanol solution.
2. Turn on the Zahner station and connect the red and green wires to the anode and the black and blue to the cathode current collectors.
3. Switch on the Thales USB and select I/E option and choose the galvanostatic mode. Leave the cell at the OCV for 15 min to stabilise and measure the OCV.
4. Impose the current intensity according to the current increments selected, let the stabilise for 3 min and measure the corresponding voltage value.
5. When the voltage value reaches 0.1 V, switch to "off" and put the Zahner on "stop".
6. Remove the alcohol solution from the anode reservoir and fill it with distilled water.

Concordant tests are achieved when the relative error between them is equal or less than 10%. In addition, it is important to record the operating temperature.

For the polarisation measurements it was selected the galvanostatic mode since the OCV of the cell is not known *a priori*, due to methanol crossover.

The EIS measurements were performed following the procedure:

1. Filled the reservoir with the methanol solution.
2. Select the EIS option, set the time between each test (3 min), the selected voltage values (0.4 V; 0.3 V and 0.2 V) and the desire frequency range (10 mHz-100 kHz).
3. Select the potentiostatic mode, an amplitude of 10 mV and the first voltage value, usually the higher one, 0.4 V.
4. Let stabilise for 15 min at the OCV and then switch to “on”.
5. When the measurement is completed, remove the alcohol solution from the reservoir and fill it with distilled water.

4 Results and discussion

In order to reduce the mpDMFC costs without a significant loss of performance, it was studied the effect of using Pt catalysts supported on carbon with different loadings on the cathode side of a mpDMFCs. On the anode side, considering the knowledge already acquired by the research team in these systems, a commercial Pt-Ru catalyst was used with a loading of $3 \text{ mg}\cdot\text{cm}^{-2}$ in all the tests performed. These catalysts were prepared in the LSRE-LCM laboratory. Therefore, to evaluate the effectiveness of the technique used to prepare the “handmade” electrodes, the cell behaviour with these electrodes was compared to the one obtained with commercial electrodes at CEFT. After validating the deposition procedure, the effect of pressing the MEA on the cell performance using “handmade” and commercial electrodes was studied. Based on the commercial electrodes available in the laboratory, these two studies were performed with a cathode catalyst of $0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 %, being the mass fraction referred to the metal. Based on the results obtained in these studies, the effect of using different catalyst loadings and support on the cathode side of a mpDMFC was evaluated. All the studies were performed with different methanol concentrations, as this parameter, as a clear effect on the methanol crossover rate and, consequently, on the cell efficiency.

The results were analysed and discussed based on the polarisation and EIS measurements, and a set of results that represent the other ones were chosen to be presented in this chapter. The remaining results can be found in Appendix B.

4.1 Effect of MEA preparation

To study the effect of the MEA preparation on the mpDMFC performance the method used to perform the catalyst deposition on the DL was evaluated. The airbrush method, and the effect of pressing the MEA were tested. As mentioned, the electrodes prepared in the LSRE-LCM were compared to commercial ones purchased at Fuel Cell Store, having a cathode catalyst loading of $0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 % and carbon cloth with a MPL as DL. The membrane used was Nafion® 117 and was pre-treated before pressing. The anode electrode used, was a commercial one, having a loading of $3 \text{ mg}\cdot\text{cm}^{-2}$ Pt-Ru and carbon cloth with a MPL as DL. The electrodes, commercial and “handmade”, were tested in the mpDMFC with and without pressing the MEA, and different methanol concentrations. The power density achieved in each condition and methanol tested are presented in Table 4.1 and the polarisation curves for a methanol concentration of 6 M, one of the concentrations that lead to higher performances, can be found in Figure 4.1. The remaining results can be found in Appendix B.2. In Table 4.1 the results in bold stand for the maximum power density achieved with the electrode studied, and is also possible to state at which concentration this happened.

Table 4.1 - Effect of the MEA preparation on the mpDMFC power output.

Methanol concentration /M	Cathode catalyst: 0.5 mg·cm ⁻² Pt/C 60%			
	Maximum power density / mW·cm ⁻²			
	Commercial	Commercial Pressed	LSRE-LCM	LSRE-LCM Pressed
1	0.19	0.56	0.28	0.4
2	0.32	0.68	0.42	0.6
3	0.40	0.77	0.43	0.66
4	0.40	0.76	0.48	0.83
5	0.41	0.94	0.57	0.96
6	0.73	1.24	0.86	1.37
7	0.81	1.77	0.90	1.12
8	0.68	1.70	0.99	-
9	-	-	1.08	-
10	-	-	0.94	-

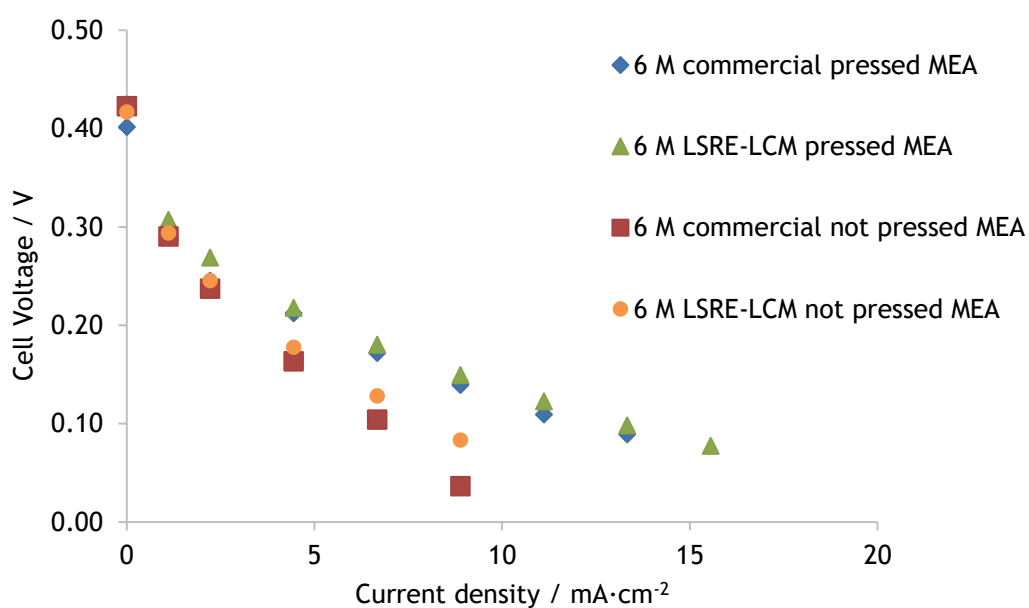


Figure 4.1 - Effect of the MEA preparation on the cell performance for commercial and LSRE-LCM electrodes.

Analysing the results presented in Table 4.1 and Figure 4.1 it is possible to state that the electrodes prepared in LSRE-LCM had similar or in the same conditions better performances than the commercial ones.

For the MEA not pressed, the maximum power density obtained for the commercial electrode was $0.81 \text{ mW}\cdot\text{cm}^{-2}$ for a methanol concentration of 7 M and for the electrode prepared in the LSRE-LCM was $1.1 \text{ mW}\cdot\text{cm}^{-2}$ for a methanol concentration of 9 M. This difference in performance can be related to the metallic dispersion or even to catalyst the particle size, as these are important factors to achieve better or worst performances. In addition, the electrode prepared allow working the cell with a methanol concentration of 10 M, while for the commercial one it was only possible to reach 8 M [6, 33, 43].

One justification for these results is the fact that when analysing visually the commercial electrode, it is observed that the catalyst distribution is not homogeneous throughout the electrode area ($30 \text{ cm} \times 30 \text{ cm}$) (Appendix B.2, Figure B.25). Thus, as the electrode used has only an area of 2.25 cm^2 , the probability that the catalyst distribution in this area is not homogeneous, as it depends on the place where the commercial electrode is cut. By preparing the electrodes in the laboratory, it is possible to ensure that the distribution is more homogeneous, since the catalyst is only deposited in the desired area (2.25 cm^2) (Appendix B.2, Figure B.26).

In addition, it is also assumed that the commercial catalyst in dust, used to prepare the electrode, is homogenous regarding the mass fraction of support and platinum.

In addition to the visualization analysis, the commercial and the LSRE-LCM electrodes were analysed by SEM; the images are presented in Figure 4.2 and the remaining ones in Appendix B.2.1. It was possible to assess that the quantity of platinum in the DL is very high in both electrodes and well dispersed through all the electrode area.

On the other hand, looking at Figure 4.2, it can be concluded that the platinum particle size is smaller in the lab-made electrode and more uniformly dispersed through the electrode surface area. The high dispersion of platinum is beneficial since it leads to an increase in the catalyst activity, as the agglomerates of platinum do not exist. These results allow validate the deposition method used and justify the higher performances achieved in the electrodes prepared during this work.

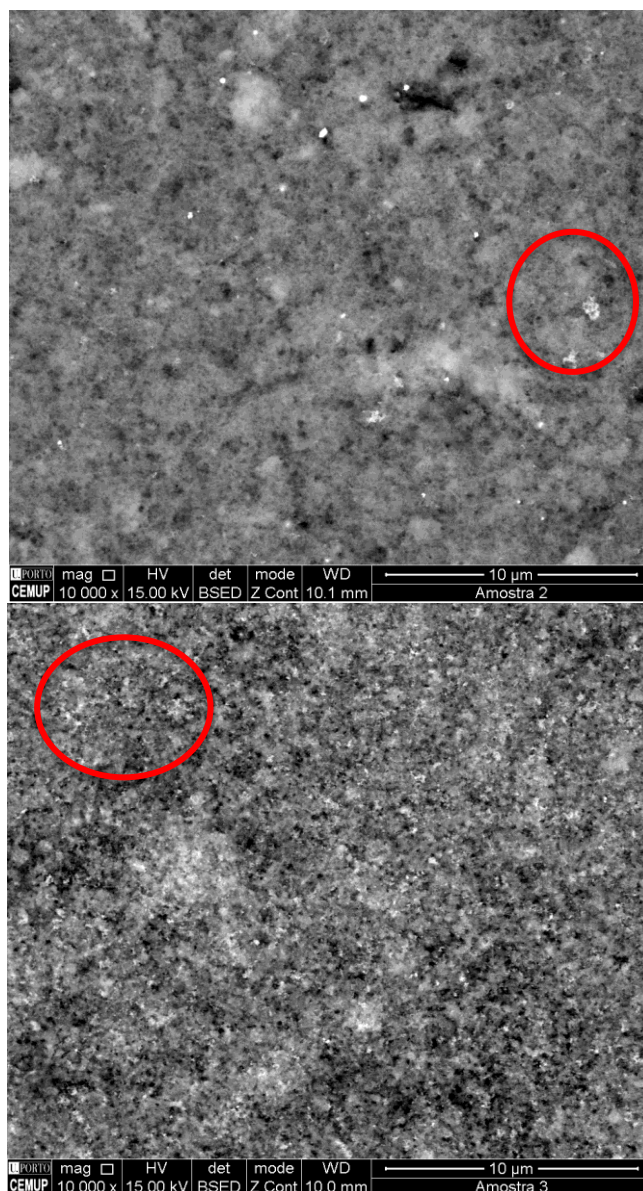


Figure 4.2 - SEM images of the commercial electrode (above) and the LSRE-LCM electrode (below).

For the electrodes with a pressed MEA, the maximum power density obtained for the commercial electrode was $1.1 \text{ mW}\cdot\text{cm}^{-2}$ for a methanol concentration of 7 M, and for the prepared electrode was $1.4 \text{ mW}\cdot\text{cm}^{-2}$ for a concentration of 6 M. Analysing the results presented in Table 4.1 and Figure 4.1, it is possible to verify that when the MEA is pressed the cell performance increases, mainly due to low resistances (Table 4.2 and Table 4.3).

The exposure of the membrane to high temperatures can lead to a degradation of the membrane in terms of its thickness, increasing the resistance to charge transport, because it decreases the proton conductivity and can increase the permeability to methanol. Although, effects on methanol permeation are not considerable as the OCV decrease in the tests with the pressed MEA is not visible, as can be seen analysing the polarisation curves. When exposed to force and high temperatures the aspect of the membrane changes, as it can be noticed in Figure

B.27 in Appendix B.2. However, the results obtained do not reflect such negative effects, since the beneficial effect of the impregnation of the catalytic layer into the membrane promotes a better contact between the Nafion® membrane and the catalytic layer, reflected on the results [58, 59].

As mentioned, EIS measurements were performed to identify and quantify, through the estimation of the cell resistances, the major losses that negatively affect the cell under study. Therefore, the EIS data was analysed using Nyquist diagrams (Figure 4.3) and an EEC (Figure 4.4) was developed and used to quantify the different losses/resistances.

Figure 4.3 shows the results obtained for the mpDMFC with a pressed MEA, a cathode electrode prepared in LSRE-LCM with a load of $0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 % and for a methanol concentration of 6 M. This experiment was chosen to be presented here as it reflects the results obtained for the other conditions tested. In Appendix B.1 is presented the other adjustments performed.

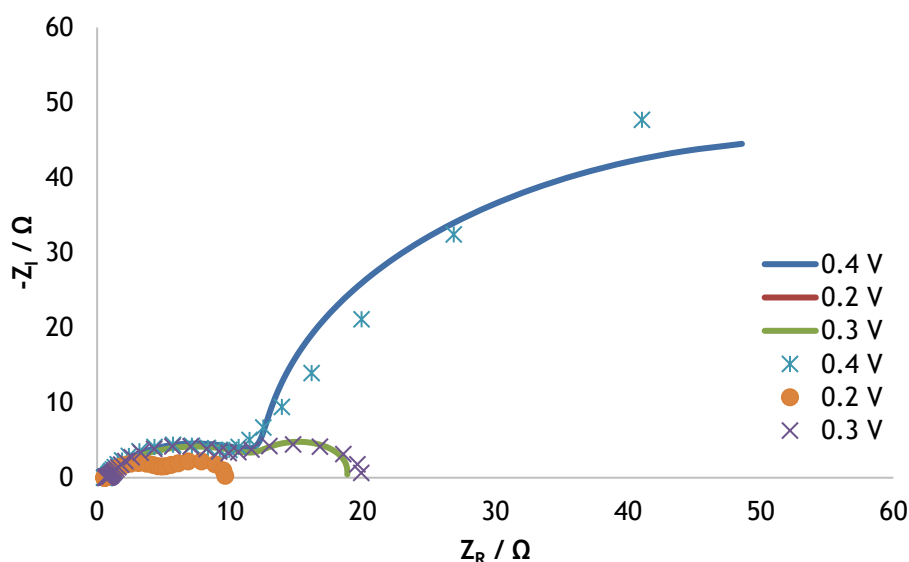


Figure 4.3 - Nyquist plots and EEC fitting for different fuel cell voltages a methanol concentration of 6 M, an electrode prepared in LSRE-LCM with $0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 % and a pressed MEA; dots: experimental data; lines: EEC fitting.

Analysing the results presented in Figure 4.3 it can be seen that the plots intercept the x -axis, the real impedance axis, in a point that represents the ohmic losses/resistance. Afterwards, it is possible to observe two arcs in the medium frequency region that have a more relevant impact for higher fuel cell voltages, characteristic behaviour of the activation losses. These results are similar to the ones obtained for the other conditions tested in the mpDFC, as well as the non-existence of losses that increase with a decrease of the cell voltage, which could represent mass transfer losses. Therefore, it can be concluded that the system under

study suffers from two activation losses. In fact, two electrochemical reactions occur in the cell: methanol oxidation (anode side) and oxygen reduction (cathode side); thus, it is expected the presence of two activation resistances. However, as both reactions have a lower rate, the losses associated with them may overlap, being very challenging to distinguish the anode and cathode activation losses.

Based on the Nyquist spectrum, the EEC that reflects the system under study is presented in Figure 4.4.

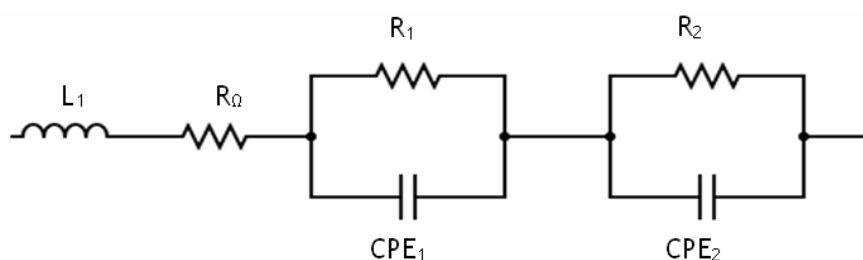


Figure 4.4 - Electric equivalent circuit adjusted to experimental data.

In Figure 4.4., L_1 represents the inductance, R_Ω refers to the ohmic resistance and R_1 and R_2 stand for the activation resistances. CPE_1 and CPE_2 represent the constant phase elements. As can be seen in Figure 4.3, the model fits the experimental results, so it reproduces the system in study and can be used to quantify the losses/resistances that affect the system.

Table 4.2 presents the values of the resistances obtained by fitting the EEC to the EIS data for a methanol concentration of 6 M, a commercial and a LSRE-LCM electrode with $0.5 \text{ mg} \cdot \text{cm}^{-2}$ Pt/C 60 % and a not-pressed MEA and Table 4.3, the results for a pressed MEA.

Table 4.2 - Effect of the electrode preparation on the cell resistances and maximum power density for a methanol concentration of 6 M and with a not-pressed MEA.

Resistances / Ω	Voltage / V	Commercial electrode	LSRE-LCM electrode
R_Ω	0.20	0.75	0.91
	0.30	0.75	0.96
	0.40	0.76	0.61
R_1	0.20	7.7	7.3
	0.30	11	11
	0.40	14	14
R_2	0.20	7.5	6.5
	0.30	21	22
	0.40	43	41
Maximum power density / $\text{mW} \cdot \text{cm}^{-2}$		0.73	0.86

As can be seen, resistances 1 and 2 increase with an increase in the cell voltage representing the activation losses. In other hand, the ohmic resistance for the commercial electrode presents a lower value than the one prepared in LSRE-LCM, but resistances 1 and 2 that are due to the electrochemical reactions, where the catalyst properties have a remarkable impact, are lower than the ones obtained with the commercial electrode. These results are in accordance with the ones presented in Table 4.1 and Figure 4.1, where better performances were achieved with the LSRE-LCM electrode.

Table 4.3 - Effect of the electrode preparation on the cell resistances and maximum power density for a methanol concentration of 6 M and a pressed MEA.

Resistances / Ω	Voltage / V	Commercial electrode	LSRE-LCM electrode
R_0	0.20	0.84	0.53
	0.30	0.85	0.54
	0.40	0.86	0.54
R_1	0.20	5.2	4.3
	0.30	6.3	7.8
	0.40	8.1	9.4
R_2	0.20	4.4	4.3
	0.30	16	18
	0.40	22	31
Maximum power density / $\text{mW}\cdot\text{cm}^{-2}$		1.2	1.4

Regarding the resistance values for a pressed MEA, it can be seen that ohmic resistances are lower for the LSRE-LCM electrode. The other resistances, resistance 1 and 2, follow the same behaviour as the one presented in the previous table, increasing with an increase of the cell voltage. Comparing the results presented in Table 4.3 and Table 4.4 it can be seen that the resistances decreased when a pressed MEA was used, since it lead to lower transport and contact resistances, between the anode and cathode electrodes and membrane.

Finally, after all the comparisons, it was possible to validate the catalyst deposition technique with the airbrush on the GDL, prepared in LSRE-LCM laboratory. Moreover, it was concluded that pressing the MEA enhanced the mpDMFC performance, so it is a necessary step to assemble the fuel cell being used in the following tests.

4.2 Effect of cathode catalyst properties

The cathode catalyst properties, namely its costs, are among the different barriers that still constrain the commercialisation of pDMFCs. To obtain satisfactory performances, it is necessary to use platinum catalysts with higher loadings, $4 \text{ mg}\cdot\text{cm}^{-2}$, which means a large amount of platinum and consequently a higher cost. As mentioned, the use of carbon supports can allow reducing the amount of platinum, promoting better performances at lower catalyst loadings. Thus, different loadings and metal/support mass fractions were studied on the cathode side of the mpDMFC to reduce the amount of metal used without compromising the performance.

4.2.1 Catalyst loading

Before analysing the effect of using a supported catalyst, it is important to analyse the effect of the catalyst loading on the cell performance. Therefore, it was prepared and tested catalyst with different loadings, operating the mpDMFC with different methanol concentrations. The power density achieved in each condition tested is presented in Table 4.4 and the polarisation curves for a methanol concentration of 4 M can be found in Figure 4.5. The remaining results can be found in Appendix B.3.

Table 4.4 - Effect of the catalyst loading on the mpDMFC power output.

Methanol concentration /M	Cathode catalyst: Pt/C 60%		
	Maximum power density / $\text{mW}\cdot\text{cm}^{-2}$		
	$0.5 \text{ mg}\cdot\text{cm}^{-2}$	$2 \text{ mg}\cdot\text{cm}^{-2}$	$4 \text{ mg}\cdot\text{cm}^{-2}$
1	0.40	2.6	2.2
2	0.60	3.6	3.9
3	0.66	4.4	5.0
4	0.83	5.6	7.0
5	0.96	6.8	8.1
6	1.37	6.9	8.8
7	1.12	4.6	6.1

In Figure 4.5 is shown the polarisation curves obtained for 0.5, 2 and 4 $\text{mg}\cdot\text{cm}^{-2}$ for Pt/C 60 % with pressed MEAs and a methanol concentration of 4 M and in Table 4.5 the cell resistances estimated by fitting the EEC to the EIS data. As the loading of 0.5 $\text{mg}\cdot\text{cm}^{-2}$ lead to very low and insufficient performances, the results will be analysed only for loadings of 2 and 4 $\text{mg}\cdot\text{cm}^{-2}$.

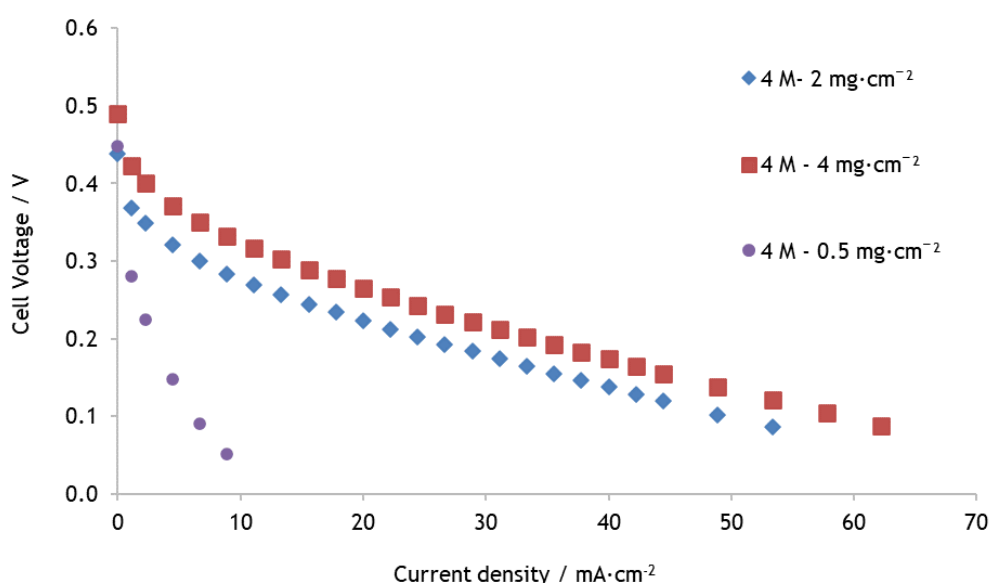


Figure 4.5 - Effect of catalyst loading on the cell performance for a methanol concentration of 4 M, a pressed MEA and a supported catalyst, Pt/C 60 %.

Analysing Figure 4.5 is perceptible that higher loadings lead to higher performances, since lead to an increase in the amount of platinum on the cathode and, consequently, more active sites are available for the ORR. Additionally, due to the methanol oxidation reaction that occurs at the cathode side, due to methanol crossover, some of the cathode catalyst active sites will be used for this reaction decreasing the available ones for the ORR. Therefore, higher loadings will help on overcoming these phenomena, achieving better performances.

Table 4.5 - Effect of the catalyst loading on the cell resistances and maximum power density achieved for a methanol concentration of 4 M, a pressed MEA and a supported catalyst.

Catalyst load	R_0 / Ω			R_1 / Ω			R_2 / Ω			Maximum power density / $\text{mW}\cdot\text{cm}^{-2}$
	0.2 V	0.3 V	0.4 V	0.2 V	0.3 V	0.4 V	0.2 V	0.3 V	0.4 V	
2 $\text{mg}\cdot\text{cm}^{-2}$ Pt/C 60 %	0.52	0.53	0.53	0.69	0.86	1.0	1.2	3.5	19	5.6
4 $\text{mg}\cdot\text{cm}^{-2}$ Pt/C 60 %	0.43	0.43	0.44	0.67	1.1	1.1	0.96	1.8	10	7.0

Analysing Table 4.5, it is visible that the resistances due to activation losses, resistance 1 and 2, are lower for higher loadings due to an enhancement of the electrochemical reaction rate, which are in accordance with the polarisation curves, where higher loadings led to higher performances.

4.2.2 Catalyst support

To study the effect using a supported catalysts at the cathode side of a mpDMFC, two different mass fractions of platinum were studied, 60 % and 40 %, which corresponds to 40 % and 60 % of support, respectively. As mentioned before, the support used was Vulcan XC-72, a type of carbon black. The power density achieved in each condition and for the different methanol concentrations tested is presented in Table 4.6 and the remaining results can be found in Appendix B.3. By the results presented in Table 4.6, it is visible that the supported catalysts allowed working under high methanol concentrations without major losses on the cell performance.

Table 4.6 - Effect of using supported catalysts on the mpDMFC power output.

Methanol concentration /M	Cathode catalyst				
	Maximum power density / $\text{mW}\cdot\text{cm}^{-2}$				
	$2 \text{ mg}\cdot\text{cm}^{-2}$ PtB	$2 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 %	$2 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 40 %	$4 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 %	$4 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 40 %
1	1.4	2.6	0.5	2.2	1.8
2	2.2	3.6	1.1	3.9	2.5
3	3.1	4.4	2.7	5.0	2.8
4	3.1	5.6	4.2	7.0	4.6
5	4.5	6.8	4.4	8.1	5.2
6	5.2	6.9	4.7	8.8	6.6
7	5.4	4.6	5.0	6.1	5.7
8	4.7	-	5.3	-	-
9	-	-	5.1	-	-
10	-	-	-	-	-

In Figure 4.6, the polarisation curves obtained for the supported and unsupported catalysts with $2 \text{ mg}\cdot\text{cm}^{-2}$ and a methanol concentration of 4 M are shown.

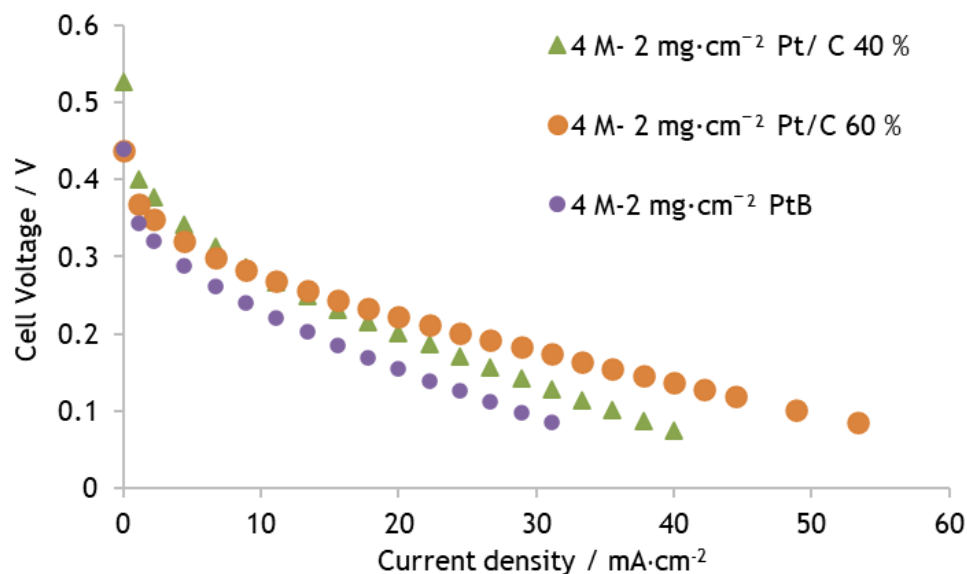


Figure 4.6 - Effect of using supported catalysts on the cell performance for a catalyst load of $2 \text{ mg}\cdot\text{cm}^{-2}$ and a methanol concentration of 4 M.

Analysing Figure 4.6, it is possible to verify that, in comparison with the catalyst without support (PtB), the cell performance was enhanced when using a supported catalyst with 60% of Pt. However, at 40 % of Pt, the cell performance decreased.

As mentioned, using carbon materials with a high surface area and crystallinity as support can provide a higher dispersion of the Pt, increasing the electron transfer rate and, consequently, the cell performance. The high conductivity of the carbon materials, used as support can also justify the enhancement in the cell performance. However, the high specific surface area provided by using a support led to small pore sizes, which may restrict the oxygen and water transport. Additionally, carbon materials can become unstable and easily oxidized in the fuel cells environment. This can lead to an agglomerate or detachment of the catalyst particles from the electrode leading to a platinum dissolution and reduction of cell performance [60]. This was verified when the amount of support used increased to 60 %. Therefore, it is necessary to achieve an optimised balance between the advantages and disadvantages of using carbon supports.

The same study was performed with a catalyst load of $4 \text{ mg}\cdot\text{cm}^{-2}$ and in Figure 4.7 are shown the polarisation curves obtained for the supported and unsupported catalysts with $4 \text{ mg}\cdot\text{cm}^{-2}$ and a methanol concentration of 4 M.

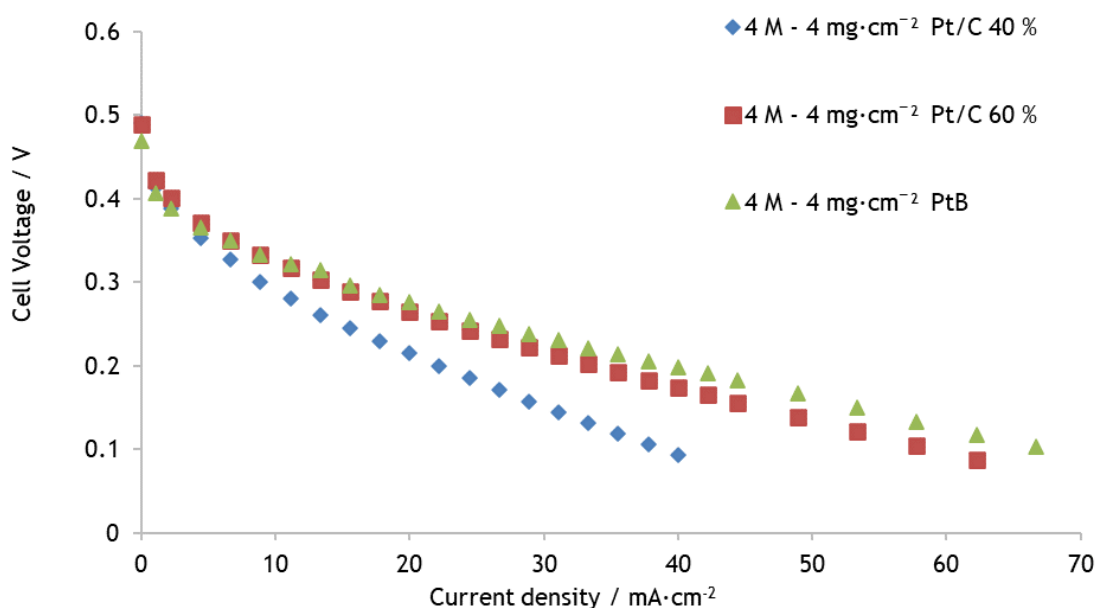


Figure 4.7 - Effect of using supported catalysts on the cell performance for a catalyst load of $4 \text{ mg}\cdot\text{cm}^{-2}$ and a methanol concentration of 4 M.

Analysing Figure 4.7 is possible to conclude, that, at a 4 M methanol concentration, the cell performance had decreased in comparison to the unsupported catalyst when used the supported catalysts, but with a very small difference. It is also visible that the performance decreased when the mass fraction of platinum was reduced from 60 % to 40 %. However, these results do not invalidate the possible positive effects of using supported catalysts, not least because the results were significantly good with supported catalysts.

Table 4.7 presents the cell resistances estimated by fitting the EEC to the EIS data for all the catalysts tested.

Table 4.7 - Effect of using supported catalysts on the cell resistances and maximum power density achieved for methanol concentration of 4 M.

Catalyst load	R_0 / Ω			R_1 / Ω			R_2 / Ω			Maximum power density / $\text{mW}\cdot\text{cm}^{-2}$
	0.2 V	0.3 V	0.4 V	0.2 V	0.3 V	0.4 V	0.2 V	0.3 V	0.4 V	
$2 \text{ mg}\cdot\text{cm}^{-2}$ PtB	0.46	0.47	0.46	1.2	1.7	2.6	2.1	7.4	21	3.1
$2 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 %	0.52	0.53	0.53	0.69	0.86	1.0	1.2	3.5	19	5.6
$2 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 40 %	0.40	0.40	0.41	2.0	3.0	3.5	1.4	3.3	20	4.2
$4 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 %	0.35	0.35	0.33	0.65	0.68	0.80	0.69	1.9	15	7.0
$4 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 40 %	0.46	0.48	0.39	0.71	0.78	1.1	1.3	2.1	9.9	4.6

The results presented in Table 4.7 are in accordance with the ones already presented, as the condition that leads to a higher performance, 2 mg·cm⁻² Pt/C 60 % and 4 mg·cm⁻² Pt/C 60 %, present lower resistance values. The high conductivity of the carbon black, used as support lead to lower ohmic resistances, as can be shown with the results for 2 mg·cm⁻² Pt/C 40 %. However, this reduction is not sufficient to overcome the disadvantages of using lower amounts of metal that will reduce the reaction rates, increasing the activation losses (R_1 and R_2).

4.3 Performance vs Cost

From the results presented in the previous section, it was concluded that using carbon supported platinum-based catalyst, normally used in cathode, has enhanced the performance of the mpDMFC, especially when using a mass fraction of 40 % of support in the catalyst. The support could not only enhance the activity of the catalyst and the dispersion of the Pt nanoparticles, but also allows the reduction of the platinum used and, in consequence, a reduction in the catalyst cost. The increase in performance may not be very significant, but considering the application for which the mpDMFC will be used, it may enable a reduction in the amount of platinum to be used and therefore reduce its cost.

Taking into consideration that to prepare an electrode with a supported platinum catalyst, the quantity in the dust of the catalyst used is higher, since to the same load of the active phase, the mass fraction of support is added to the metal. So, a higher fraction of support leads to a higher mass of catalyst dust needed to be used to prepare the catalysts. In Table 4.8 is shown the prices of the different catalysts used. To obtain these prices, were considering the price of platinum black and the price of Vulcan XC-72, purchased at Fuel Cell Store, and the mass fraction of which one [61, 62].

Table 4.8 - Prices for the different catalysts used on the electrode preparation.

Catalyst	Price / €·g ⁻¹
Platinum Black / 100 % Pt	168
Vulcan XC-72	0.91
60 % Pt; 40% Vulcan XC-72	101
40 % Pt; 60% Vulcan XC-72	68

With this preliminary study, the prices are only considering the reagents prices. However, for a more detailed analysis, it should be necessary to consider other additional costs, such as the impregnation of the catalyst into the support.

Analysing the prices of the dust already prepared for the different mass fractions of metal, it is visible that the price decrease with the decrease of platinum content. In Figure 4.8 is shown the relation between the different loadings of catalyst and mass fraction of platinum used in tests with the maximum power density obtained for each test. To perform the calculations were used the mass of the catalyst used to prepare each one of the electrodes that can be found in Table A.1 in Appendix A.2.

It is visible that the price to prepare the electrode with the catalyst with lower platinum content is higher. It happens since the mass of the dust needed is higher to achieve the same platinum load.

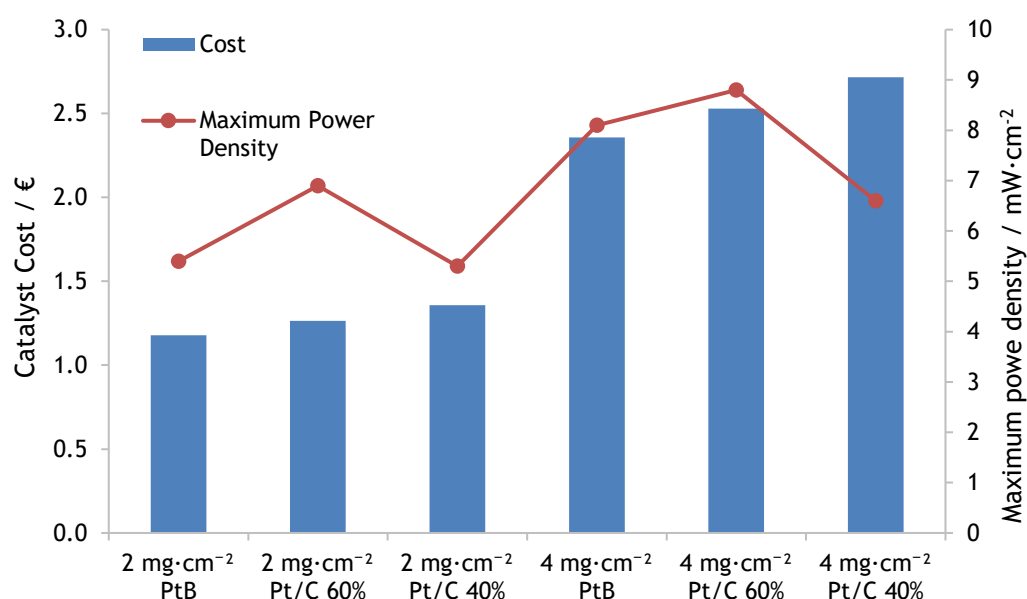


Figure 4.8 - Representation of the catalyst cost for each electrode prepared and the maximum power density obtained for each one.

As shown in Figure 4.8, the power density achieved with 2 mg·cm⁻² is lower than the ones obtained with 4 mg·cm⁻² supported catalyst, but the reduction in the catalyst cost is very significant. Considering a cost-to-power analysis, it could be considered that using a loading of 2 mg·cm⁻² Pt/C 60 % in detriment of the standard loading of 4 mg·cm⁻² allows for reducing the cost associated with the catalyst, achieving a higher performance that can be sufficient for some applications.

The power density achieved with a 2 mg·cm⁻² Pt/C 60 % can be lower than the ones obtained with a loading of 4 mg·cm⁻² with support, but with 60 % in mass of metal the enhanced performance and the reduced cost compared with a higher loading could compensate since the power density obtained is close to the value of the ones with a loading of 4 mg·cm⁻². Thus, using at the cathode side a catalyst with 2 mg·cm⁻² Pt/C 60 % is very attractive towards achieving the cost-effectiveness needed for these systems.

4.4 Effect of methanol concentration

The optimum methanol concentration consists in the concentration at which the cell reaches its maximum power density. In this section the influence of alcohol concentration on the mpDMFC performance is presented for the condition tested that lead to the best compromise between the catalyst cost and the cell performance. As concluded in the previous sections, this was achieved with a pressed MEA and an electrode prepared in LSRE-LCM with $2 \text{ mg} \cdot \text{cm}^{-2}$ Pt/C 60 % as cathode catalysts. Figure 4.9 shows the polarisation curves for all the concentrations studied (1-7). As for a methanol concentration of 7 M the performance was lower than the one obtained for 6 M, this was the last concentration tested. The power density curves can be found in Appendix B.4.

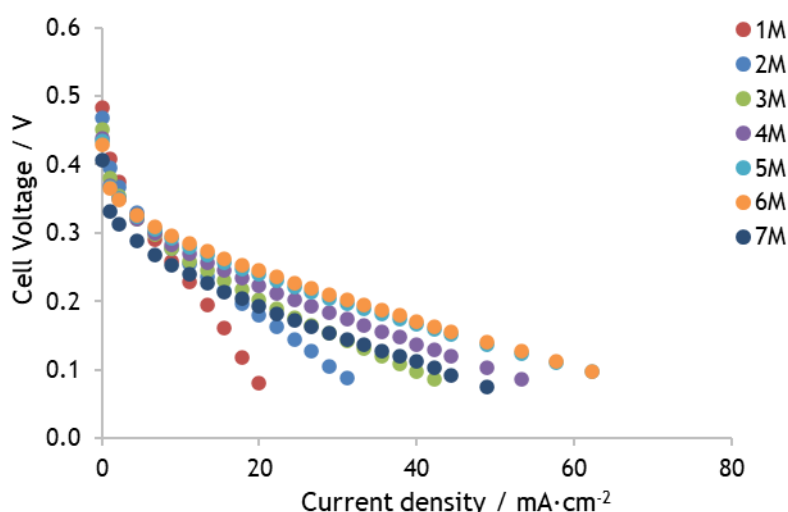


Figure 4.9 - Polarisation curve for the study of the methanol concentration.

By analysing Figure 4.9 it was verified that the cell had a higher performance at 6 M with a maximum power density of $6.89 \text{ mW} \cdot \text{cm}^{-2}$. As the methanol solutions used are dilute solutions, when the cell works at high concentrations, the amount of water is lower, i.e., there is more methanol available for the MOR and consequently more energy is produced, and the possibility of cathode flooding is also reduced. The fact that the cell can operate at higher concentrations shows that the catalysts activity is higher.

However, increasing the concentration also increases the methanol crossover rate, due to an increase in the methanol concentration gradient between the anode and the cathode side, which is not favourable to the cell performance since it results in a decrease of methanol available in the anode side to react. Moreover, the methanol that reaches the cathode, reacts at the cathode catalysts, blocking the catalyst active sites and decreasing their availability to the ORR. Additionally, in the test performed with high methanol concentration it was verified the formation of CO_2 bubbles on the anode side and water drops on the cathode side (Appendix

B.4, Figure B.49 and B.50), which can block the reactants access to the reaction zone, decreasing the cell efficiency.

Observing Figure 4.9 it is possible to assess that the OCV is much lower than the ideal voltage and, as expected, decreases with an increase in the methanol concentration, due to an increase on the methanol crossover rate. It is also visible that the cell limiting current increases with an increase on the methanol concentration, leading to higher performances.

Table 4.9 presents the resistances obtained by fitting the EEC to the EIS data for a methanol concentration of 2 M and 6 M. The values for the remaining concentrations can be found in Appendix B.4.

Table 4.9 - Resistance values and maximum specific power for the study of methanol concentration.

Concentration / M	Voltage / V	R_0 / Ω	R_1 / Ω	R_2 / Ω	Maximum power density / $\text{mW}\cdot\text{cm}^{-2}$
2	0.20	0.48	1.4	2.0	3.6
	0.30	0.49	1.4	4.1	
	0.40	0.49	1.8	15	
6	0.20	0.35	0.65	0.69	6.9
	0.30	0.35	0.68	1.9	
	0.40	0.33	0.80	15	

Analysing the values of the ohmic resistance it is possible to assess that, as expected, the values do not change significantly with the methanol concentration, since the concentration does not have a direct effect on the charge transport. The resistances 1 and 2 stand as activation losses as explain before, and as can be seen in Table 4.9, R_2 have a higher value than R_1 , for both concentrations. As the higher methanol concentration led to a higher performance the losses that affect the system are lower and consequently R_1 and R_2 have lower values. Analysing the resistance values for the highest voltage tests, 0.4 V, where the crossover losses are dominant, it can be seen that R_2 is much higher than R_1 . Considering that the methanol crossover as a relevant effect on the cathode side due to the formation of a mixed potential at this side and cathode poisoning it is expected that the losses/resistance at the cathode is higher than at the anode side, indication that R_2 , may be associated with the cathode activation losses.

To conclude, increasing the methanol concentration increases the power density of the cell but, on the other hand, decreases the open circuit voltage and increases the methanol crossover. Thus, as crossover is a phenomenon difficult to avoid, a balance is required for the cell to have a higher performance with the lowest possible impact from crossover.

For the cell under study the best concentration, the one that leads to a proper balance between the positive and negative effects of an increase on the methanol concentration on the cell performance, is 6 M.

Finally, in Table B.12 of Appendix B.4 the maximum power density obtained for each configuration studied and the power at which this occurred can be observed. Although the concentration value may vary, it can be assumed that a 6 M concentration represents an optimum point of operation.

5 Conclusion

The demand for technologies that are less polluting and can supply electrical energy to different applications in a sustainable way has been increasing. Thus, direct methanol fuel cells, namely the passive ones, are a promising solution to supply electrical energy to portable applications due to their simplicity and easy handling. However, the high cost associated with these cells, mainly due to the catalysts and loadings used to achieve an acceptable power output, hinders its commercialisation on a large scale. Having this in mind, this dissertation focused on studying the influence of using a platinum catalyst supported on carbon at the cathode side of these cells on the cell performance towards reducing the amount of platinum used, reducing the associated costs. For that, it was necessary to prepare the cathode electrodes in LSRE-LCM and validate the deposition method in the DL as well as the effect of the MEA pressing in the cell performance. All the results were analysed using polarisation and power density curves and impedance measurements performed at CEFT.

Concerning the MEA preparation, it was concluded that the method used to perform the catalyst deposition on the DL, using an airbrush, was the most appropriate one since the electrodes prepared during this work presented a very similar or even higher performance than the commercial ones. Regarding the MEA pressing, a better performance was obtained with pressed MEAs, so it is recommended to perform that before assembling the mpDMFC.

Regarding the study of the effect of the cathode catalyst properties, it was verified, as expected, that the cell performance improves when using higher platinum loadings, namely $4 \text{ mg}\cdot\text{cm}^{-2}$. However, when using a carbon supported catalyst it was possible to achieve performances that could meet some of this technology market targets with a reduction of the catalyst cost. Based on the results obtained, it was possible to verify that adding the catalyst to a support improves the platinum dispersion and the catalyst activity. The high conductivity of the carbon support can also justify the increase in performance. Thus, the best power outputs achieved with supported catalysts were $6.9 \text{ mW}\cdot\text{cm}^{-2}$ with $2 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C and $8.8 \text{ mW}\cdot\text{cm}^{-2}$ with $4 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C both with a platinum mass of 60 %. When performing a cost-to-power analysis, it was concluded that the power reached with the electrode with a cathode catalyst of $2 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 % lead to a cost-effectiveness more attractive than those obtained with higher loadings.

Finally, it was concluded that with the “handmade” electrodes, it was possible to work with high methanol concentrations, 6 M being the best methanol concentration for the system under study, mpDMFC.

6 Assessment of the work done

6.1 Objectives Achieved

The main objectives of this dissertation were to analyse the effect of using a catalyst supported on carbon at the cathode side of mpDMFCs towards a cost reduction and without a significant loss of efficiency. As shown, this goal was fully achieved since it was verified that it can be used in low-cost catalysts with attractive performances and higher methanol concentrations. It was also possible to validate the electrode and MEA preparation methods, as the cell behaviour with the developed electrodes was similar or even higher than those obtained with commercial electrodes and the SEM analysis showed similar characteristics between them.

6.2 Final Assessment

Fuel cells are one of the most promising solutions when it comes to a sustainable electrical energy production and the realisation of this dissertation allowed not only obtaining a deep knowledge of these systems, but also increase the interest in this field, namely in developing electrocatalysts, which are crucial for achieving higher performances and lifetime, with attractive costs and efficiencies.

As the electrodes preparation and its evaluation on the mpDMFC behaviour consumed a significant amount of time, only the platinum mass fractions of 60 % and 40 % were studied for two Pt loadings $4 \text{ mg}\cdot\text{cm}^{-2}$ and $2 \text{ mg}\cdot\text{cm}^{-2}$. To compare the electrodes performance with and without support, it was prepared an electrode with $4 \text{ mg}\cdot\text{cm}^{-2}$ PtB and $2 \text{ mg}\cdot\text{cm}^{-2}$ PtB and its behaviour was analysed in the mpDMFC.

As verified in this work, studying different catalysts and types of supports is crucial to achieving higher performances and lower costs. So, it would be important to test more support mass fractions, such as 20 % and 80 %, to fully understand the support impact on the cell efficiency. It will also be interesting to test other catalysts supports, such as CNT and other platinum loadings at the cathode side.

A more detailed characterization of the electrodes, in addition to the SEM analysis, will be mandatory to understand the effect of the catalyst layer thickness, surface area, and to obtain the precise catalyst load, since there are always some errors associated with the different experimental methods.

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Appendix A - Experimental Procedures

A.1 Membrane preparation

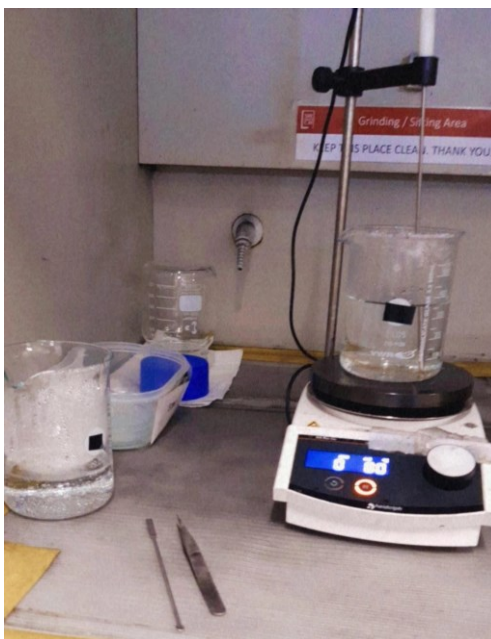


Figure A.1- Experimental setup for membrane preparation.

The H_2O_2 solution was prepared from a 30 % (V/V) solution available in the laboratory in a volumetric flask of 200 mL. So, to reach the final concentration of 3 % (V/V), 20 ml of the initial H_2O_2 solution was measured with a volumetric pipette and mixed with distilled water.

To prepare the solution of 0.5 M of H_2SO_4 the respective acid with a purity of 95 % was used. Considering a molar mass of $98.079 \text{ g}\cdot\text{mol}^{-1}$ and a density of $1.83 \text{ g}\cdot\text{cm}^{-3}$ and the fact that the solution was prepared in a volumetric flask of 200 mL, the calculations for the volume of acid used were explained below.

$$\frac{0.5 \text{ mol}}{L} \times 200 \text{ mL} \times \frac{1 L}{1000 \text{ mL}} \times \frac{98.079 \text{ g}}{\text{mol}} \times \frac{\text{cm}^3}{1.83 \text{ g}} \times \frac{1 \text{ mL}}{1 \text{ cm}^3} \times \frac{1}{95 \%} = 5.6 \text{ mL} \quad (\text{A.1})$$

A.2 Electrode preparation



Figure A.2 - Airbrush used for the catalytic depositions.

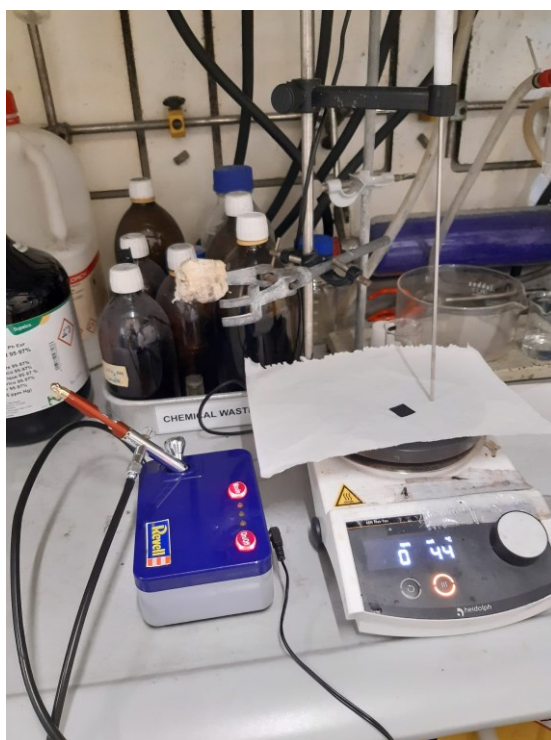


Figure A.3 - Experimental setup for the catalytic depositions.

The calculation of the catalyst mass was performed using Equation (A.2) that presents as example of the preparation of the catalyst with $0.5 \text{ mg} \cdot \text{cm}^{-2} \text{ Pt/C } 60 \%$. The remaining results are summarised in Table A.1. As using the airbrush method leads to some losses, it was used an excess of 60 % of catalyst in the dust.

$$\frac{0.5 \text{ mg Pt}}{\text{cm}^2} \times 2.25 \text{ cm}^2 \times \frac{100 \text{ mg catalyst}}{60 \text{ mg Pt}} = 1.88 \text{ mg catalyst} \quad (\text{A.3})$$

$$1.875 \text{ mg catalyst} \times 1.6 = 2.81 \text{ mg catalyst} \quad (\text{A.4})$$

Nafion 5% (pre-defined correlation) (A.5)

$$2.8125 \text{ mg catalyst} \times \frac{0.121 \text{ ml Nafion}}{30 \text{ mg catalyst}} = 11.34 \mu\text{L}$$

Isopropanol (pre-defined correlation) (A.6)

$$2.8125 \text{ mg catalyst} \times \frac{1.8 \text{ ml Nafion}}{30 \text{ mg catalyst}} = 168.75 \mu\text{L}$$

Table A.1 - Mass of catalyst, volume of the 5 % Nafion® 5 % and isopropanol used in ink preparation.

Catalyst	Catalyst Mass / g	Nafion® / μL	Isopropanol / μL	Final catalyst loading
0.5 mg·cm ⁻² Pt/C 60 %	0.003	11	168.8	0.44 mg·cm ⁻² Pt/C 60 %
0.5 mg·cm ⁻² Pt/C 60 %	0.003	11	168.8	0.50 mg·cm ⁻² Pt/C 60 %
2 mg·cm ⁻² Pt/C 60 %	0.01	48	720.0	1.7 mg·cm ⁻² Pt/C 60 %
4 mg·cm ⁻² Pt/C 60 %	0.02	97	1440.0	4.1 mg·cm ⁻² Pt/C 60 %
2 mg·cm ⁻² Pt/C 40 %	0.02	77	1147.5	1.9 mg·cm ⁻² Pt/C 40 %
4 mg·cm ⁻² Pt/C 40 %	0.04	145	2160.0	3.9 mg·cm ⁻² Pt/C 40 %
2 mg·cm ⁻² PtB	0.007	29	432.0	1.7 mg·cm ⁻² PtB
4 mg·cm ⁻² PtB	0.014	58	864.0	3.7 mg·cm ⁻² PtB

A.3 MEA pressing

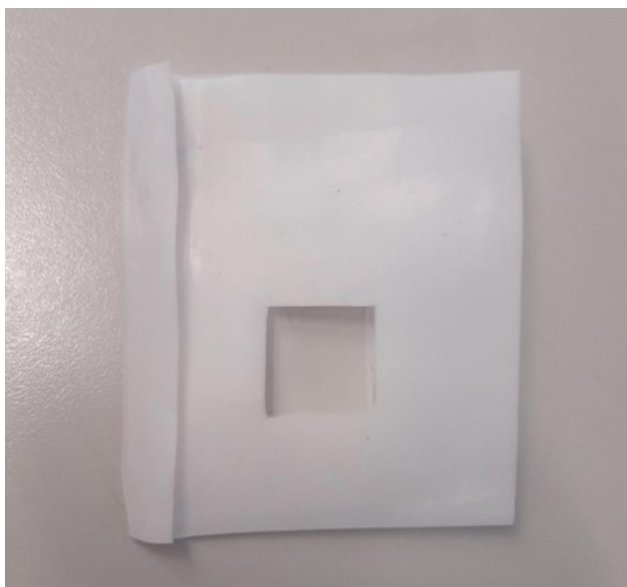


Figure A.4 - Envelope-shaped of Teflon® used in the MEA pressing.



Figure A.5 - Experimental setup for the MEA pressing.

A.4 Methanol solutions

The solutions of methanol used in the tests in the mpDMFC were prepared in volumetric flasks of 25 mL. The methanol used has a purity of 99.9 % (V/V) and was supplied by Fisher Chemical. Below is an example of the calculations done for 1 M ($\text{mol}\cdot\text{L}^{-1}$) considering a molar mass of $32.04 \text{ g}\cdot\text{mol}^{-1}$ and a density of $0.762 \text{ g}\cdot\text{cm}^{-3}$ for methanol. In Table A.2 can be found the proportions used for each concentration, that is, the volume of methanol that has been pipetted for each concentration.

$$\frac{1 \text{ mol}}{\text{L}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times 25 \text{ mL} \times \frac{32.04 \text{ g}}{\text{mol}} \times \frac{1 \text{ cm}^3}{0.762 \text{ g}} \times \frac{1 \text{ mL}}{1 \text{ cm}^3} \times 0.99 = 1.00 \text{ mL} \quad (\text{A.7})$$

Table A.2 - Methanol volumes used to prepare the different methanol concentrations tests.

Methanol concentration / mol L^{-1}	1	2	3	4	5	6	7	8	9	10
Methanol volume to be pipetted / mL	1	2	3	4	5	6	7	8	9	10

Appendix B- Results

B.1 EIS fitting

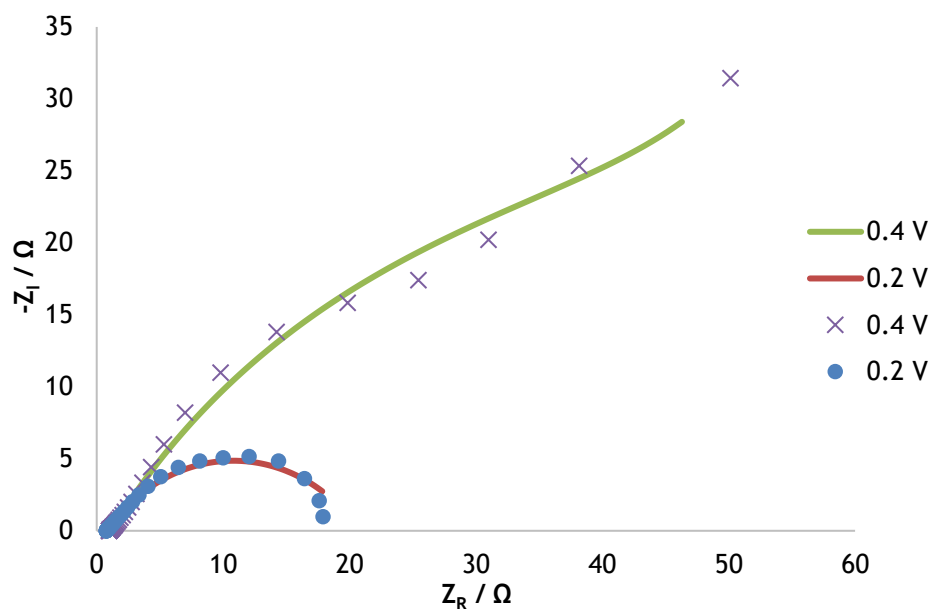


Figure B.1 - EIS spectrum for different voltages, a methanol concentration of 2 M and an electrode with a load of $0.5 \text{ mg} \cdot \text{cm}^{-2}$ Pt/C 60 % commercial.

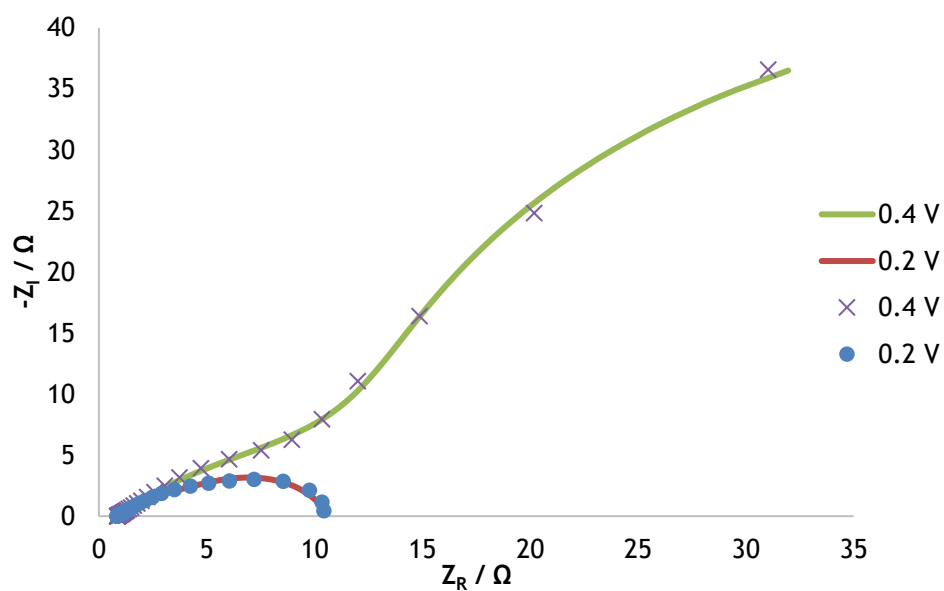


Figure B.2 - EIS spectrum for different voltages, a methanol concentration of 6 M and an electrode with a load of $0.5 \text{ mg} \cdot \text{cm}^{-2}$ Pt/C 60 % commercial.

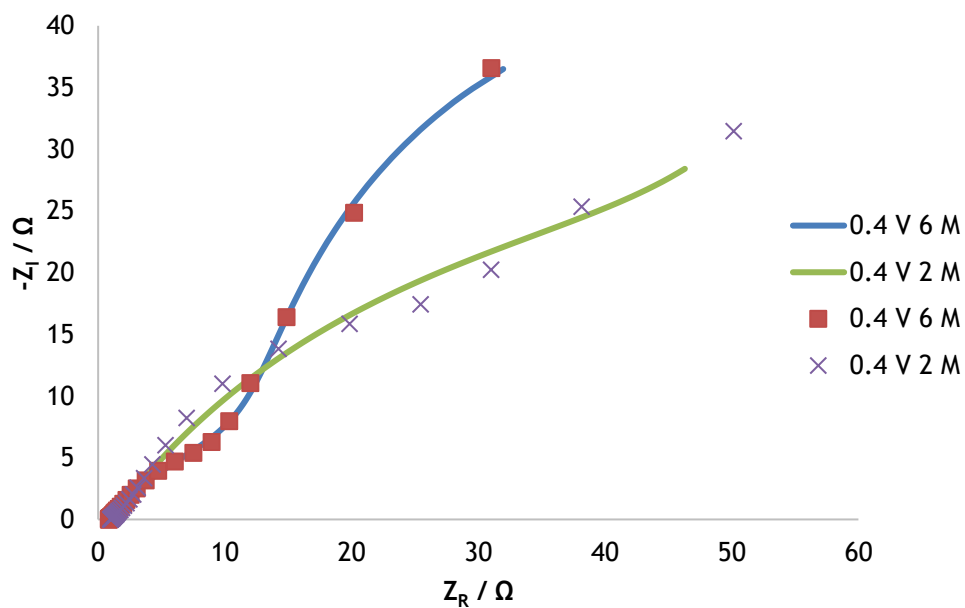


Figure B.3 - Effect of the methanol concentration on the EIS spectrum for 0.4 V and an electrode with a load of $0.5 \text{ mg} \cdot \text{cm}^{-2}$ Pt/C 60 % commercial.

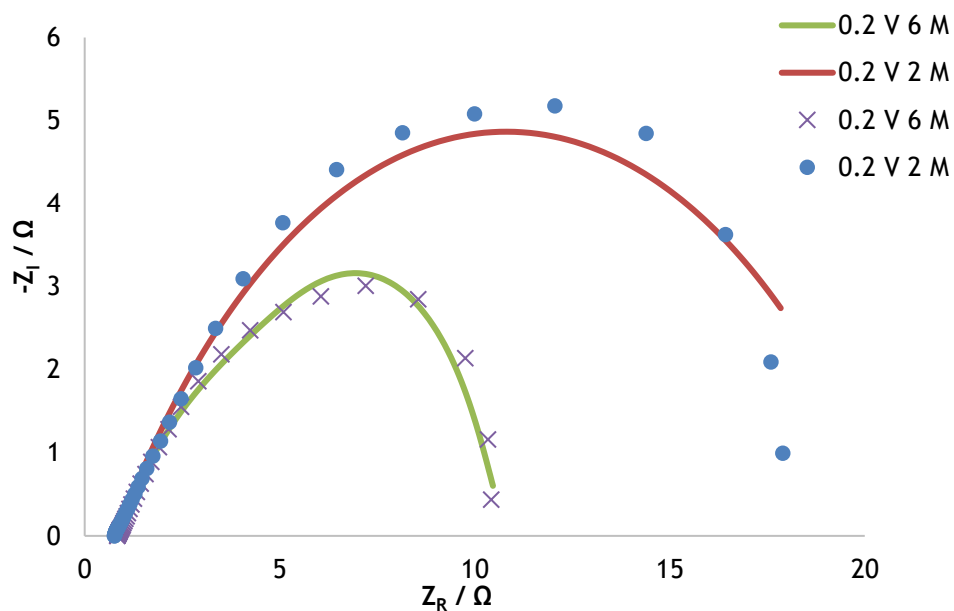


Figure B.4 - Effect of the methanol concentration on the EIS spectrum for 0.2 V and an electrode with a load of $0.5 \text{ mg} \cdot \text{cm}^{-2}$ Pt/C 60 % commercial.

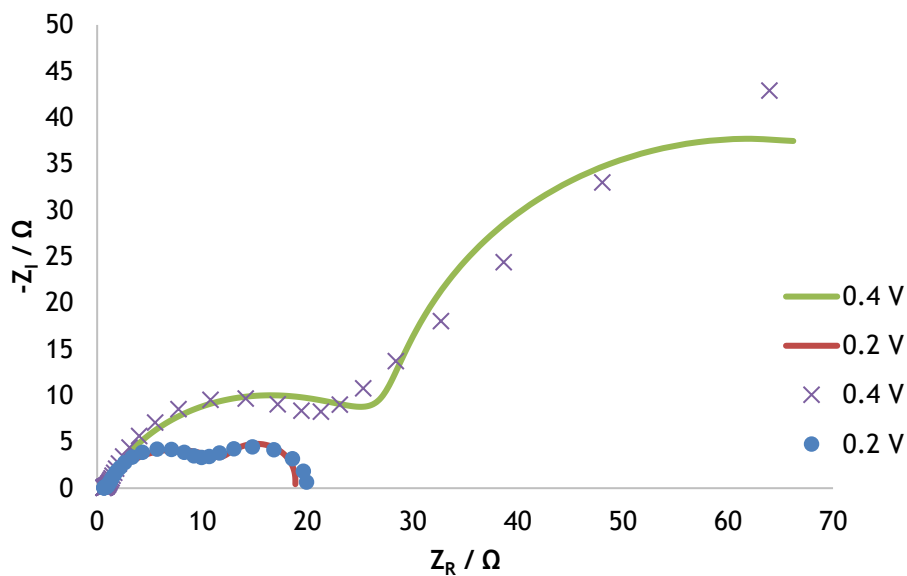


Figure B.5 - EIS spectrum for different voltages, a methanol concentration of 2 M and an electrode with a load of $0.5 \text{ mg} \cdot \text{cm}^{-2}$ Pt/C 60 % prepared in LSRE-LCM.

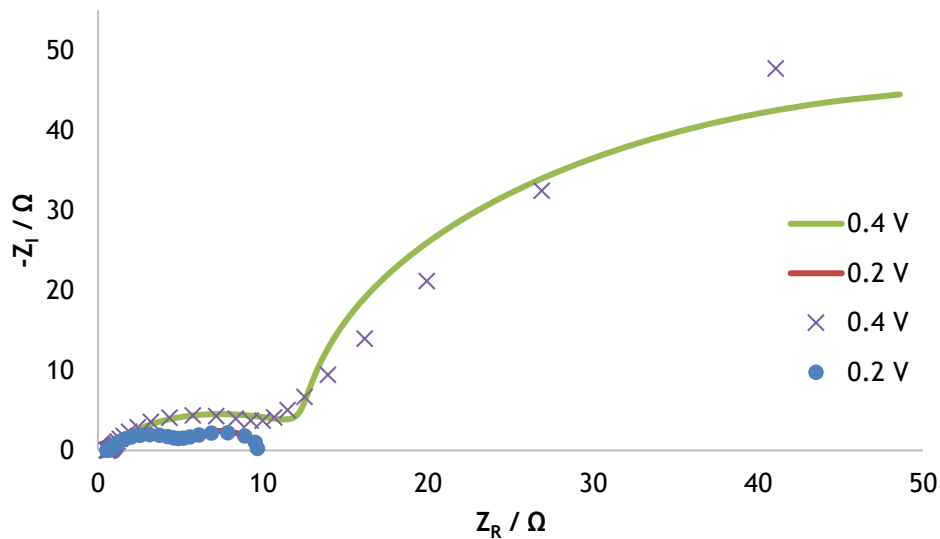


Figure B.6 - EIS spectrum for different voltages, a methanol concentration of 6 M and an electrode with a load of $0.5 \text{ mg} \cdot \text{cm}^{-2}$ Pt/C 60 % prepared in LSRE-LCM.

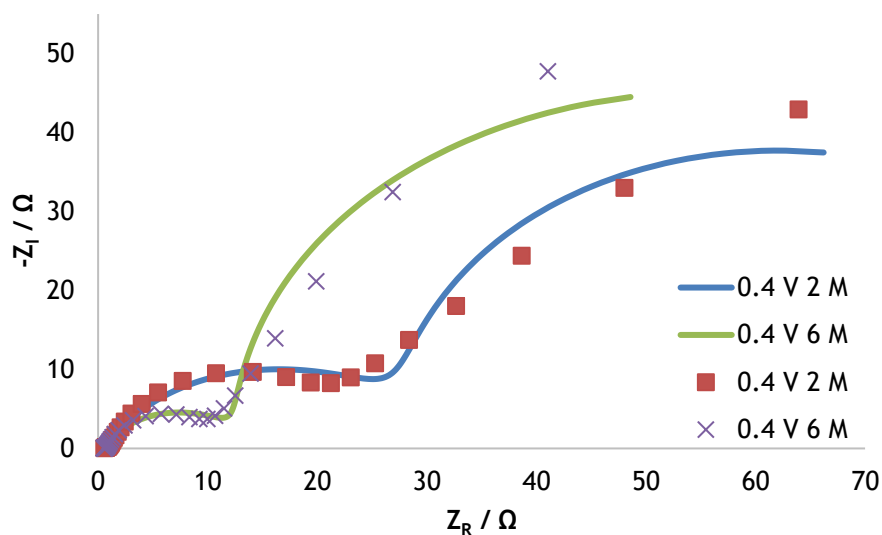


Figure B.7 - Effect of the methanol concentration on the EIS spectrum for 0.4 V and an electrode with a load of $0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 % prepared in LSRE-LCM.

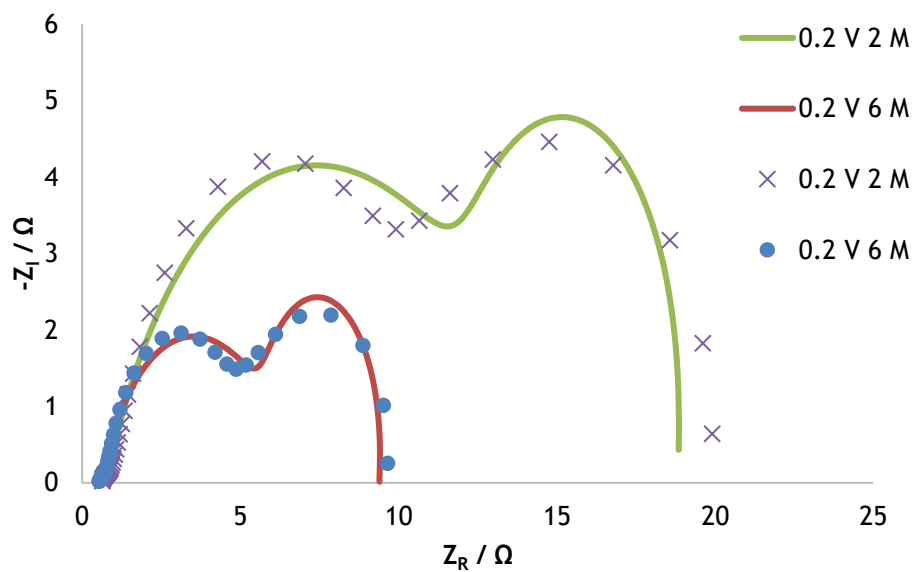


Figure B.8 - Effect of the methanol concentration on the EIS spectrum for 0.2 V and an electrode with a load of $0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 % prepared in LSRE-LCM.

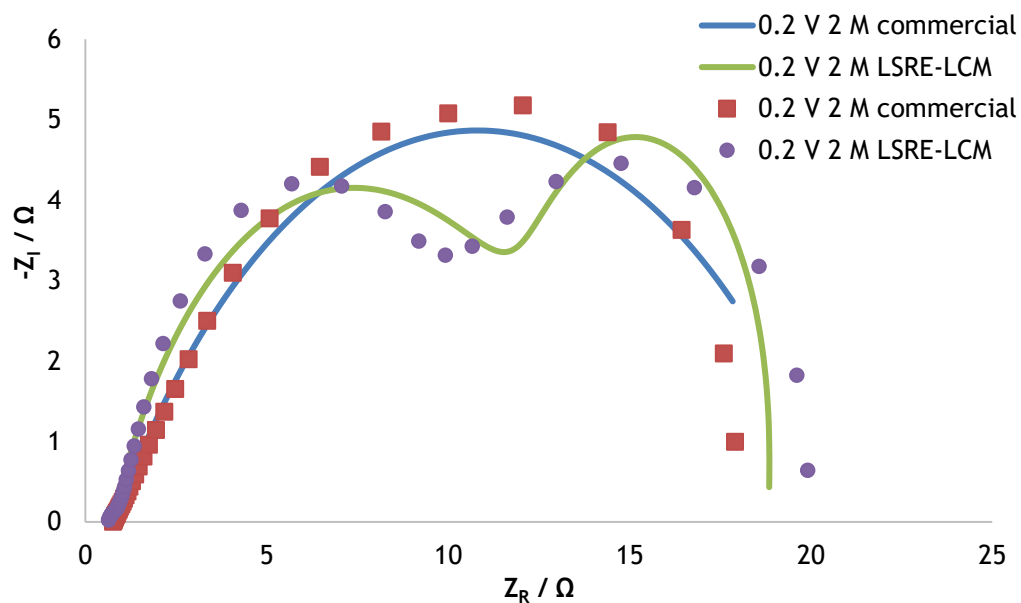


Figure B.9 - EIS spectrum for 0.2 V for a methanol concentration of 2 M and an electrode load of 0.5 mg·cm⁻² Pt/C 60 %.

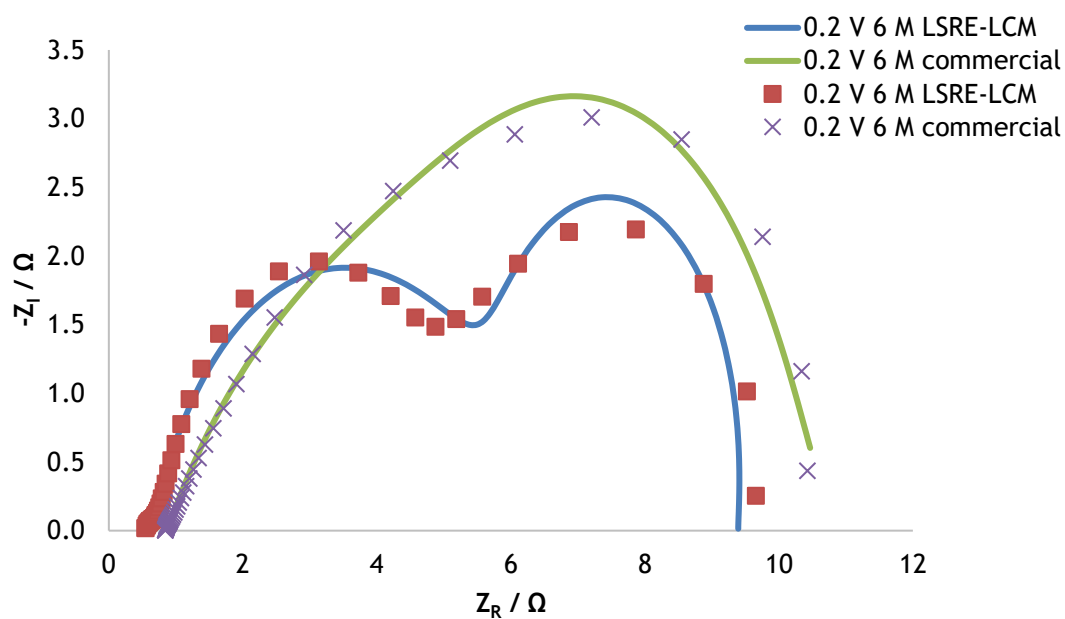


Figure B.10 - EIS spectrum for 0.2 V for a methanol concentration of 6 M an electrode load of 0.5 mg·cm⁻² Pt/C 60 %.

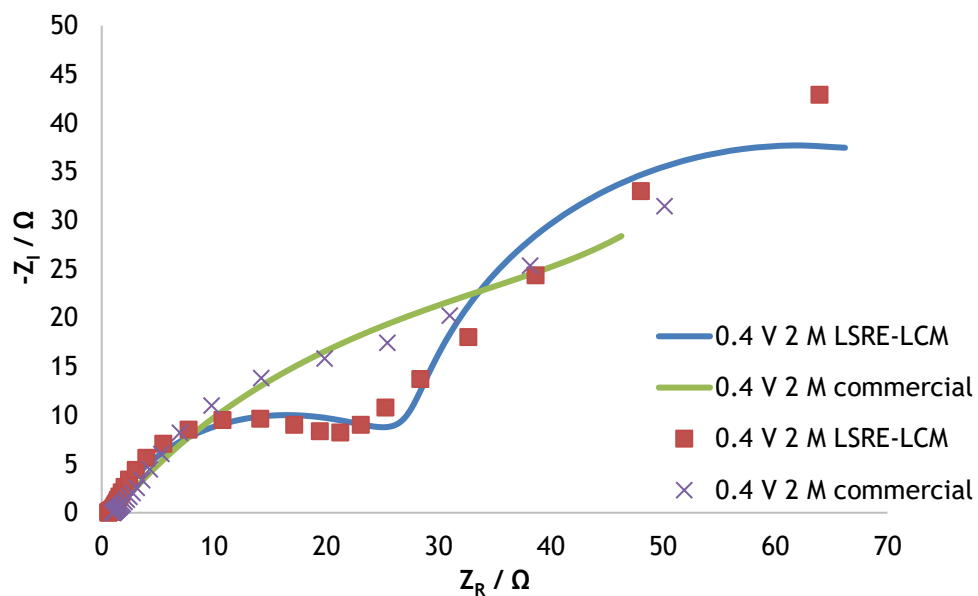


Figure B.11 - EIS spectrum for 0.4 V for a methanol concentration of 2 M and an electrode load of $0.5 \text{ mg} \cdot \text{cm}^{-2} \text{ Pt/C } 60 \%$.

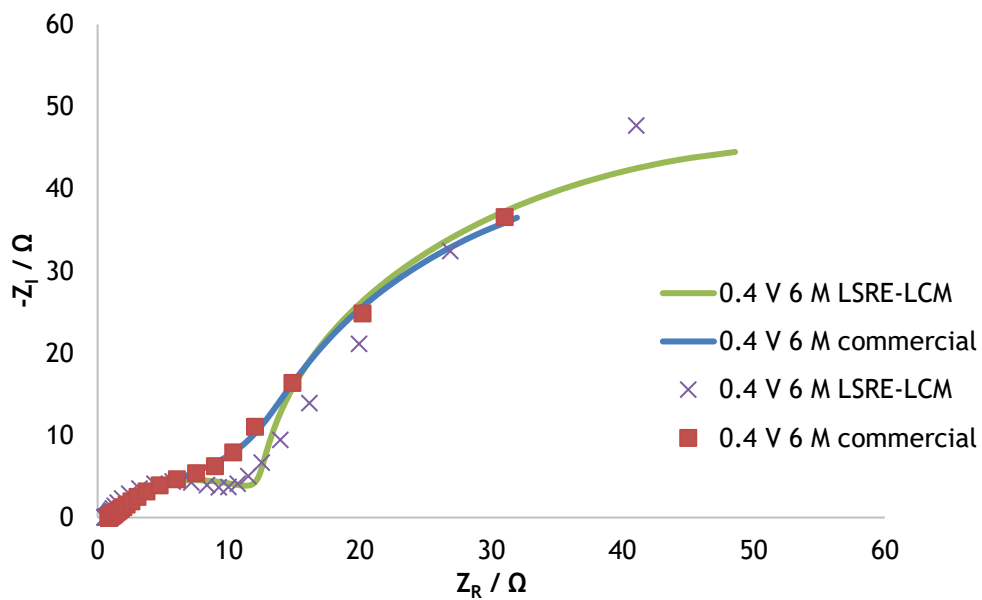


Figure B.12 - EIS spectrum for 0.4 V for a methanol concentration of 6 M and an electrode load of $0.5 \text{ mg} \cdot \text{cm}^{-2} \text{ Pt/C } 60 \%$.

B.2 Effect of MEA preparation

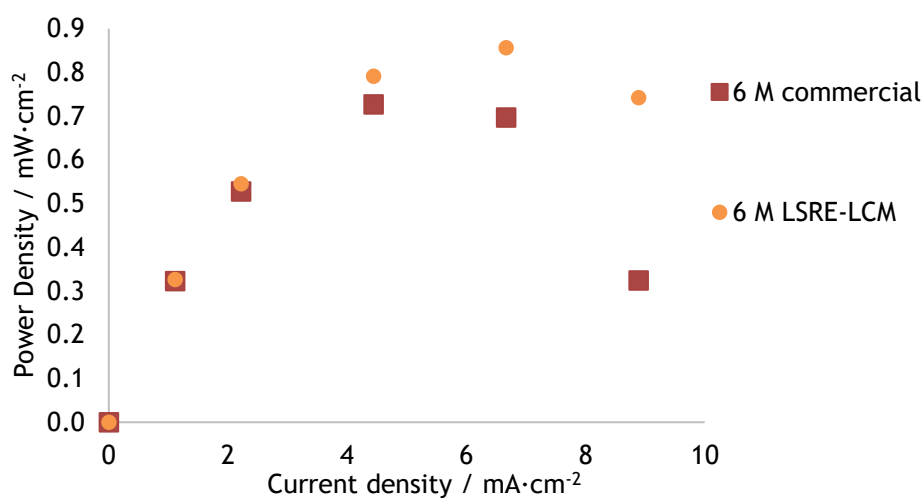


Figure B.13 - Effect of the electrode preparation on the cell power output for a catalyst load of $0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 % with a not pressed MEA.

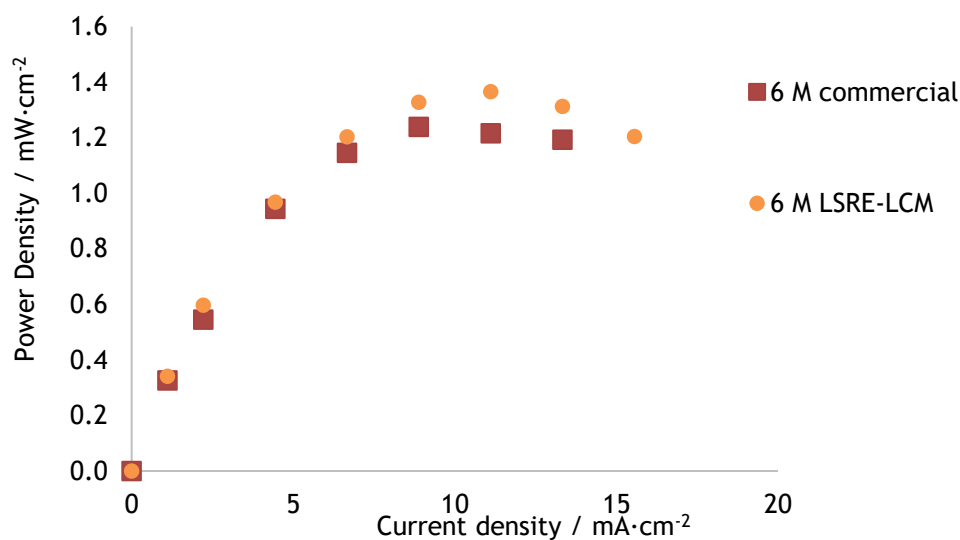


Figure B.14 - Effect of the electrode preparation on the cell power density for a catalyst load of $0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 % with a pressed MEA.

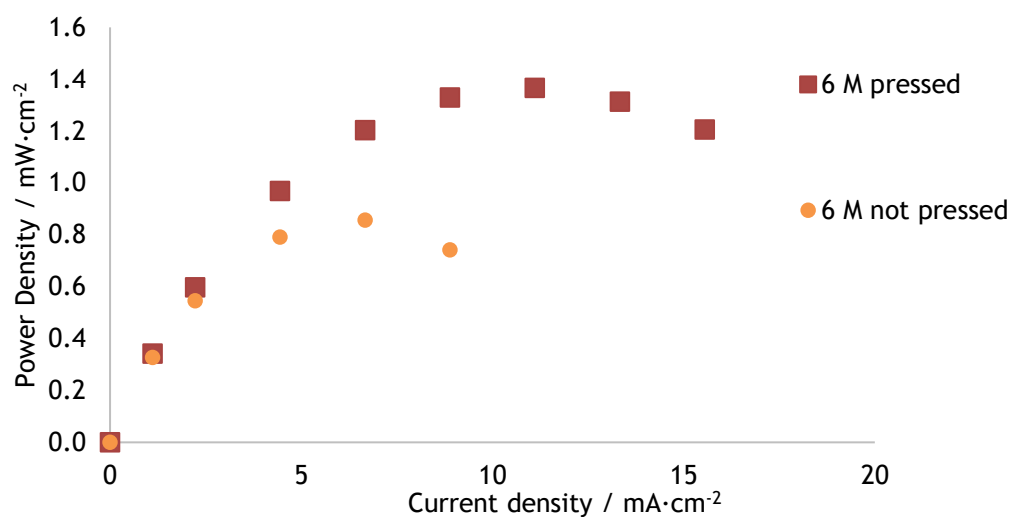


Figure B.15 - Effect of the MEA pressing on the cell power density for a catalyst load of $0.5 \text{ mg} \cdot \text{cm}^{-2}$ Pt/C 60 % in the cathode.

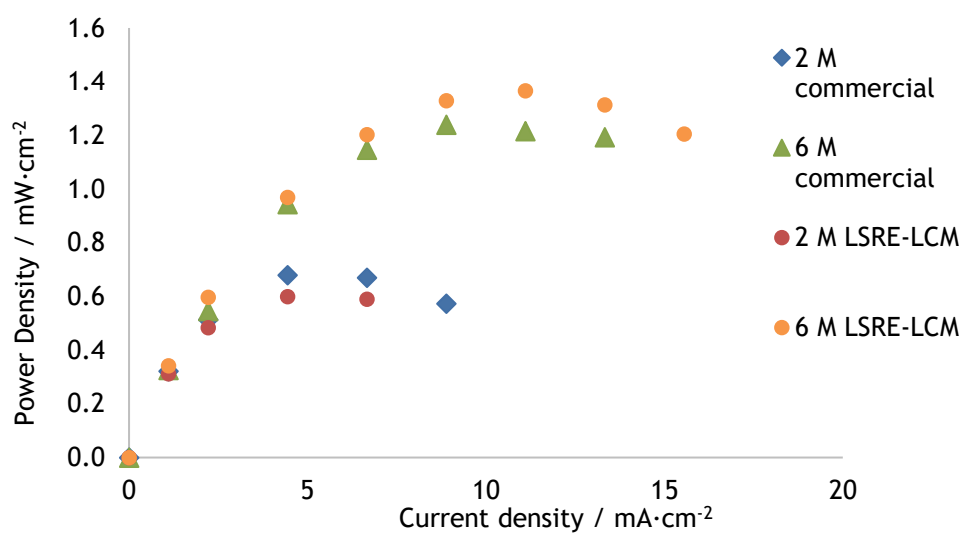


Figure B.16 - Effect of the MEA preparation on the cell power density curve for a catalyst load of $0.5 \text{ mg} \cdot \text{cm}^{-2}$ Pt/C 60 %

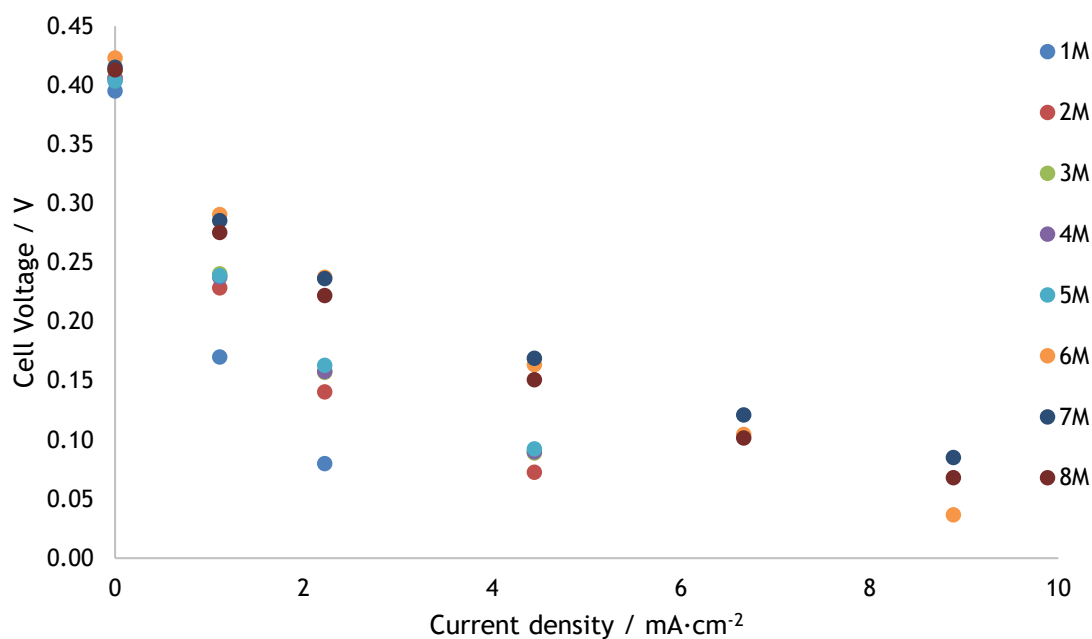


Figure B.17 - Effect of the methanol concentration on the cell performance for a cathode catalyst load of $0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 % commercial / MEA not pressed.

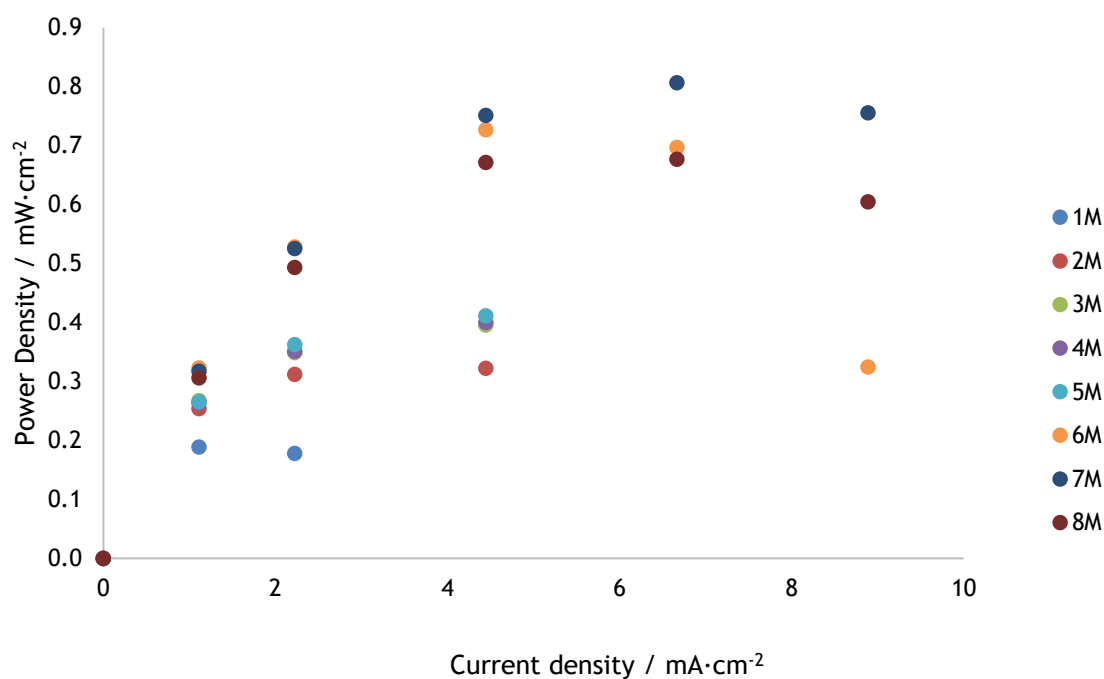


Figure B.18 - Effect of methanol concentration on the cell power density for a cathode catalyst load of $0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 % commercial / MEA not pressed.

*Table B.1 - Resistance values and maximum power density for a cathode catalyst load of $0.5 \text{ mg} \cdot \text{cm}^{-2}$
Pt/C 60 % commercial / MEA not pressed.*

Concentration / M	Voltage/ V	R_0	R_1	R_2	Maximum power density / $\text{mW} \cdot \text{cm}^{-2}$
1	0.20	0.54	27	32	0.19
	0.30	0.54	44	47	
	0.40	-	-	-	
2	0.20	0.54	16	19	0.32
	0.30	0.54	29	32	
	0.40	0.54	49	43	
3	0.20	0.62	14	16	0.40
	0.30	0.58	20	33	
	0.40	0.57	32	46	
4	0.20	0.53	14	17	0.40
	0.30	0.53	20	35	
	0.40	0.54	30	43	
5	0.20	0.58	13	16	0.41
	0.30	0.59	21	33	
	0.40	0.59	25	44	
6	0.20	0.75	7.8	7.5	0.73
	0.30	0.75	11	21	
	0.40	0.76	14	43	
7	0.20	0.58	6.9	7.5	0.81
	0.30	0.58	8.5	24	
	0.40	0.59	11	41	
8	0.20	1.7	5.4	11	0.68
	0.30	1.7	9.8	28	
	0.40	1.4	12	41	

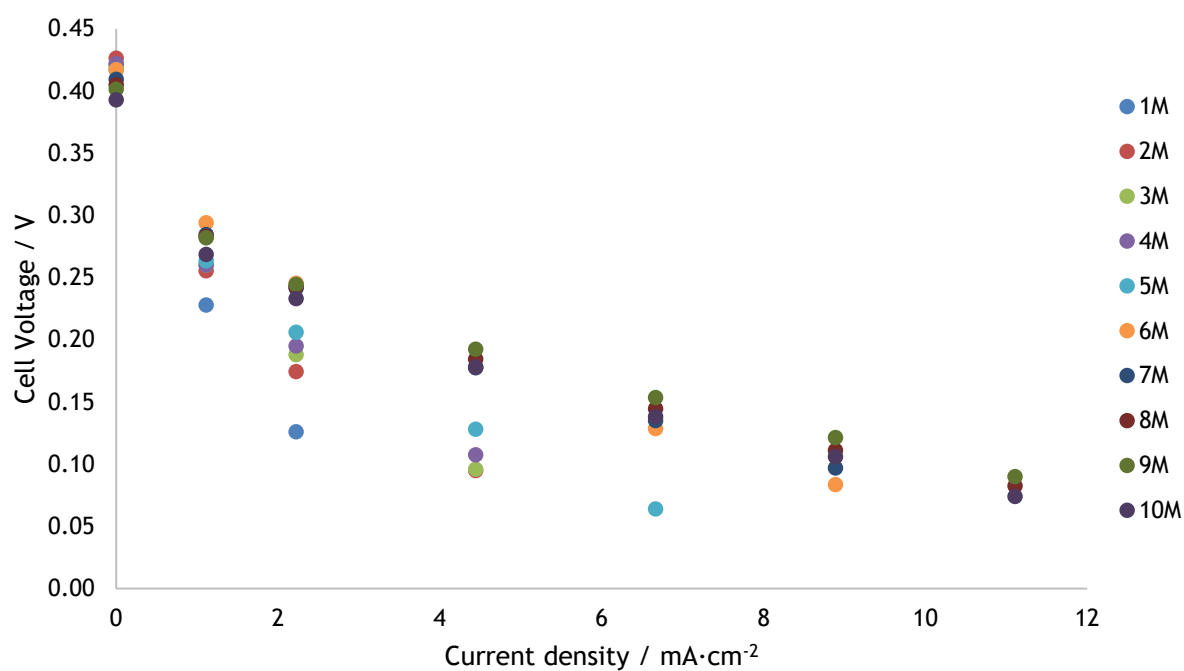


Figure B.19 - Effect of the methanol concentration on the cell performance for a cathode catalyst load of $0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 % prepared in LSRE-LCM / MEA not pressed.

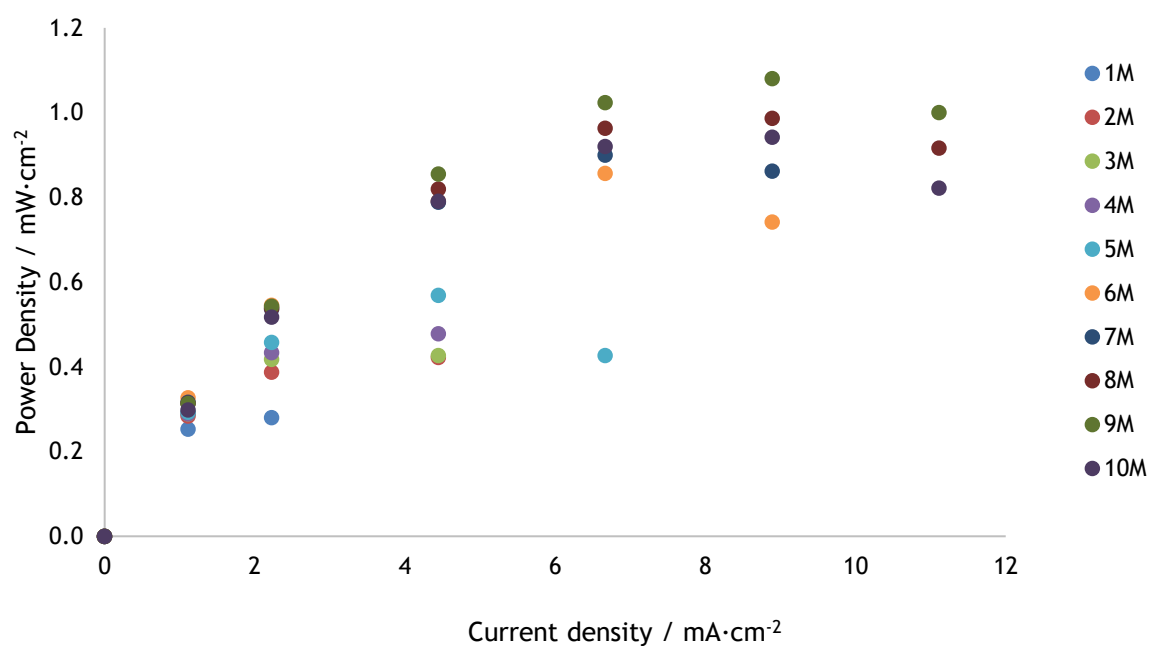


Figure B.20 - Effect of the methanol concentration on the cell power density for a cathode catalyst load of $0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 % prepared in LSRE-LCM / MEA not pressed.

*Table B.2 - Resistance values and maximum power density for a cathode catalyst load of $0.5 \text{ mg} \cdot \text{cm}^{-2}$
Pt/C 60 % prepared in LSRE-LCM / MEA not pressed.*

Concentration / M	Voltage/ V	R_0	R_1	R_2	Maximum power density / $\text{mW} \cdot \text{cm}^{-2}$
1	0.20	0.65	24	22	0.28
	0.30	0.66	30	41	
	0.40	0.66	41	56	
2	0.20	0.54	17	14	0.42
	0.30	0.54	23	30	
	0.40	0.55	30	49	
3	0.20	0.64	14	12	0.43
	0.30	0.64	21	20	
	0.40	0.77	27	46	
4	0.20	0.74	12	11	0.48
	0.30	0.74	17	30	
	0.40	0.76	21	43	
5	0.20	0.51	9.3	9.5	0.57
	0.30	0.51	14	29	
	0.40	0.52	16	40	
6	0.20	0.91	7.3	6.6	0.86
	0.30	0.96	11	22	
	0.40	0.61	14	41	
7	0.20	0.46	6.8	6.3	0.90
	0.30	0.46	10	23	
	0.40	0.46	12	40	
8	0.20	0.65	6.0	5.9	0.99
	0.30	0.65	8.9	23	
	0.40	0.66	10	38	
9	0.20	0.58	5.7	6.3	1.1
	0.30	0.59	8.1	26	
	0.40	0.59	8.5	34	
10	0.20	0.45	6.3	7.2	0.94
	0.30	0.48	8.1	32	
	0.40	-	-	-	

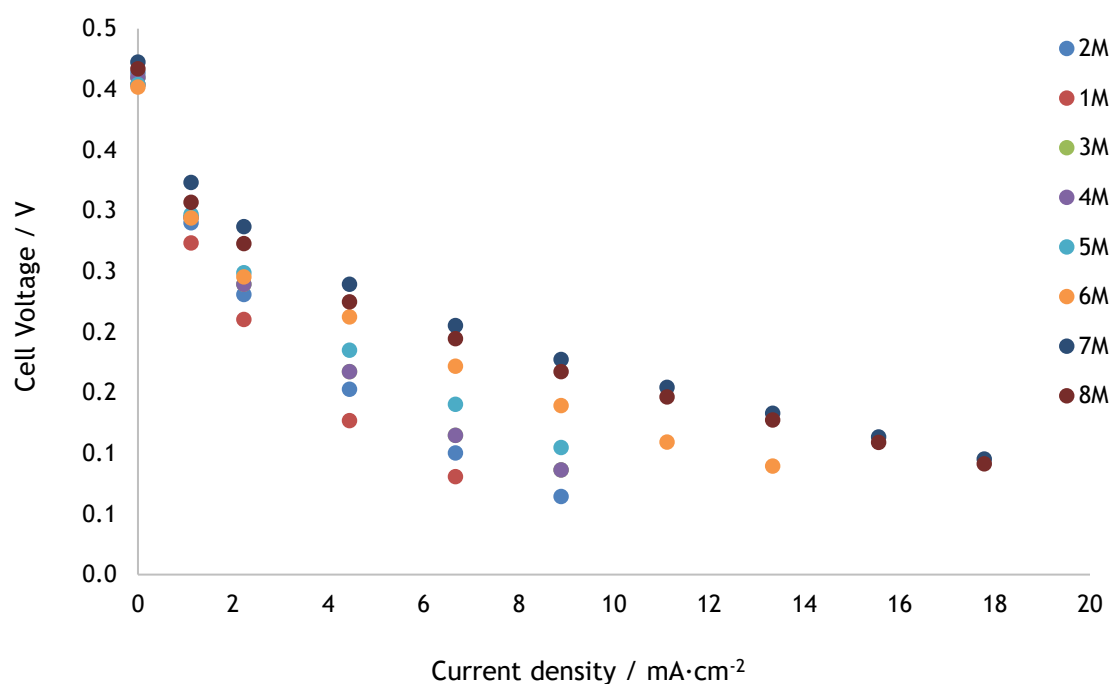


Figure B.21- Effect of the methanol concentration on the cell performance for a cathode catalyst load of $0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 % prepared in LSRE-LCM / MEA pressed.

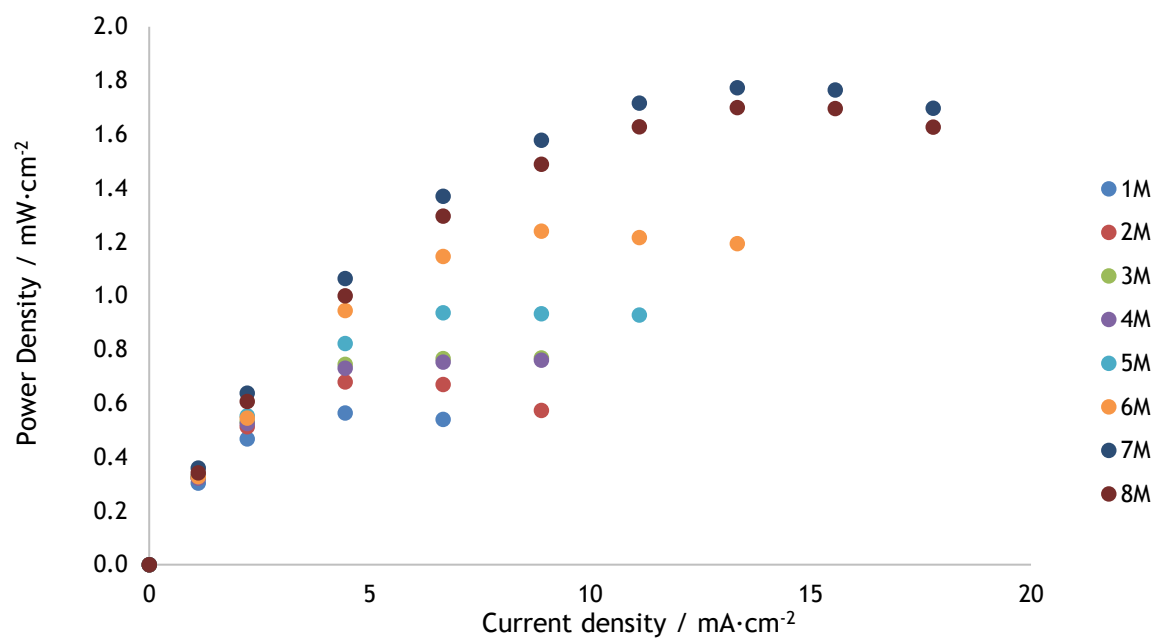


Figure B.22 - Effect of the methanol concentration on the cell power density for a cathode catalyst load of $0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 % commercial / MEA pressed.

*Table B.3 - Resistance values and maximum power density for a cathode catalyst load of $0.5 \text{ mg} \cdot \text{cm}^{-2}$
Pt/C 60 % commercial / MEA pressed.*

Concentration / M	Voltage/ V	R_0	R_1	R_2	Maximum power density / $\text{mW} \cdot \text{cm}^{-2}$
1	0.20	0.62	9.9	10	0.56
	0.30	0.58	16	20	
	0.40	0.58	30	31	
2	0.20	0.76	7.4	9.8	0.68
	0.30	0.86	15	17	
	0.40	0.99	24	25	
3	0.20	0.87	7.0	8.2	0.77
	0.30	0.87	14	17	
	0.40	0.88	21	22	
4	0.20	0.90	7.0	8.6	0.76
	0.30	0.89	11	20	
	0.40	0.92	16	24	
5	0.20	0.63	6.1	6.4	0.94
	0.30	0.63	11	15	
	0.40	0.63	13	21	
6	0.20	0.84	5.2	4.4	1.2
	0.30	0.85	6.3	16	
	0.40	0.86	8.1	22	
7	0.20	0.56	3.3	3.3	1.8
	0.30	0.54	5.1	12	
	0.40	0.56	6.6	23	
8	0.20	0.61	3.3	3.6	1.7
	0.30	0.61	5.0	14	
	0.40	0.58	6.4	22	

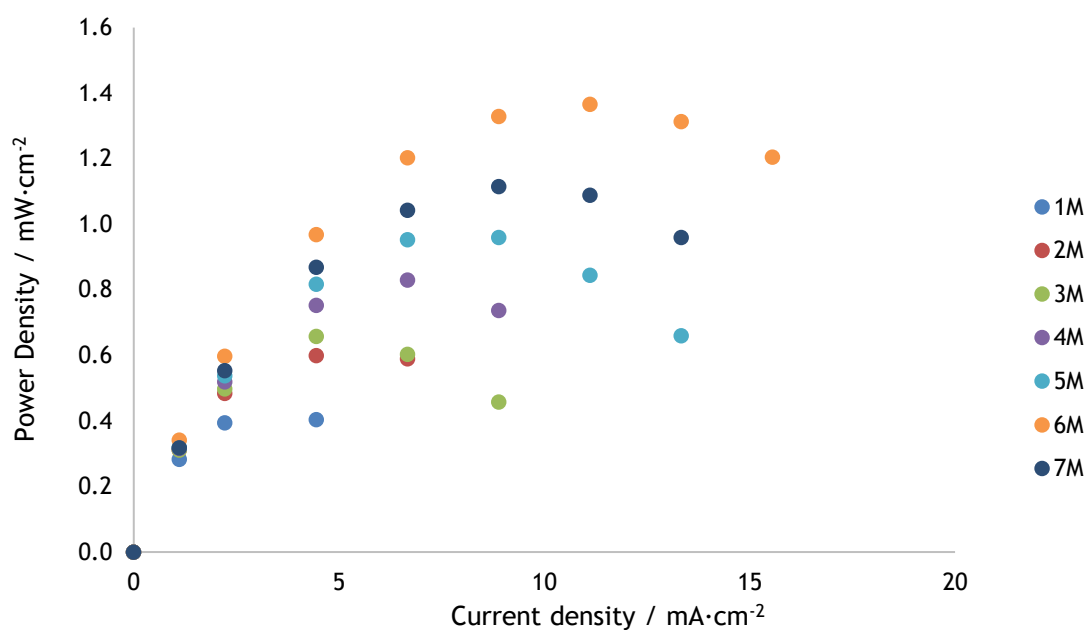


Figure B.23 - Effect of the methanol concentration on the cell performance for a cathode catalyst load of $0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 % prepared in LSRE-LCM / MEA pressed.

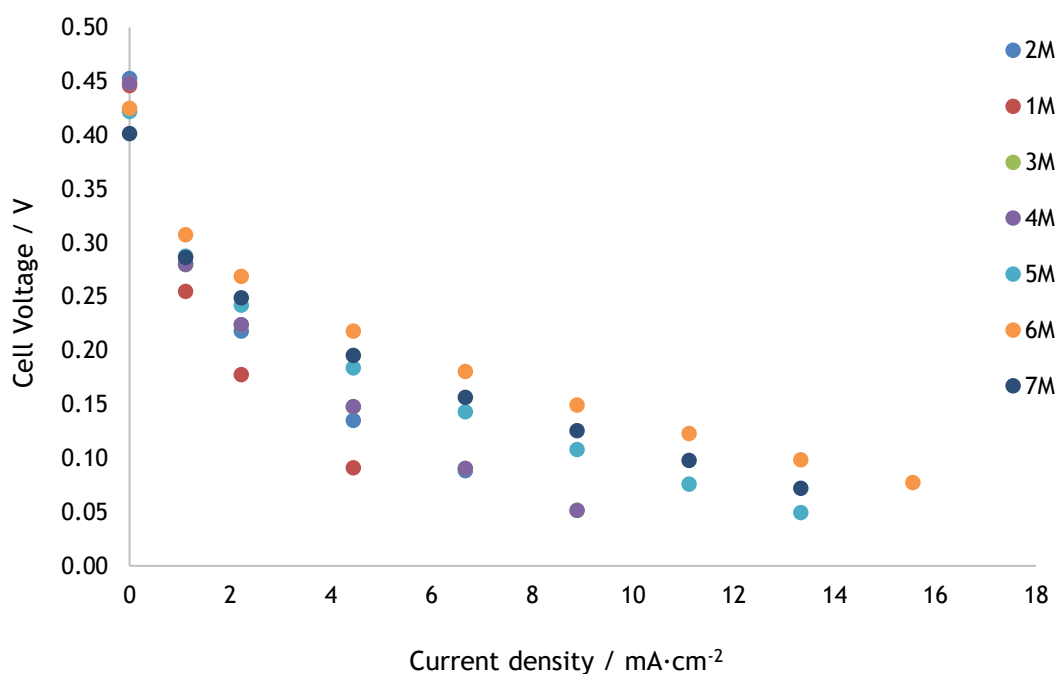


Figure B.24 - Effect of the methanol concentration on the cell power density for a cathode catalyst load of $0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 % prepared in LSRE-LCM / MEA pressed.

*Table B.4 - Resistance values and maximum power density for a cathode catalyst load of $0.5 \text{ mg} \cdot \text{cm}^{-2}$
Pt/C 60 % prepared in LSRE-LCM / MEA pressed.*

Concentration / M	Voltage/ V	R_0	R_1	R_2	Maximum power density / $\text{mW} \cdot \text{cm}^{-2}$
1	0.20	0.64	14	16	0.40
	0.30	0.65	21	33	
	0.40	0.77	28	56	
2	0.20	0.63	9.3	9.8	0.60
	0.30	0.59	15	26	
	0.40	0.59	21	43	
3	0.20	0.55	8.1	8.2	0.66
	0.30	0.54	13	24	
	0.40	0.53	17	38	
4	0.20	0.54	6.5	6.7	0.83
	0.30	0.54	11	23	
	0.40	0.54	14	33	
5	0.20	0.59	5.8	6.2	0.96
	0.30	0.60	9.3	22	
	0.40	0.48	11	33	
6	0.20	0.53	4.3	4.3	1.4
	0.30	0.54	7.8	18	
	0.40	0.54	9.4	31	
7	0.20	0.71	5.5	6.3	1.1
	0.30	0.68	9.2	26	
	0.40	0.61	12	28	

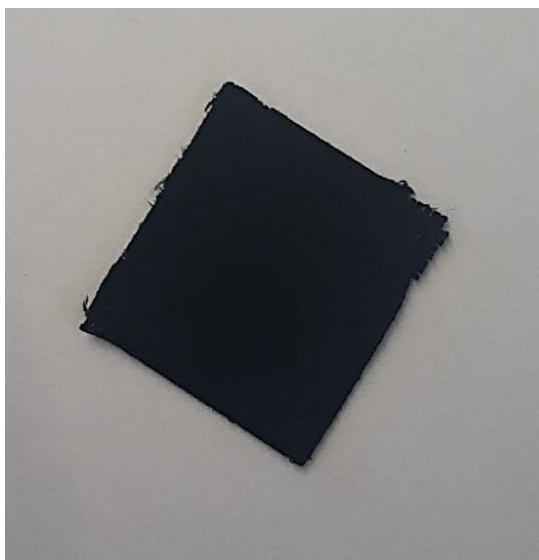


Figure B.25 - Electrode prepared in LSRE-LCM with $0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 %.

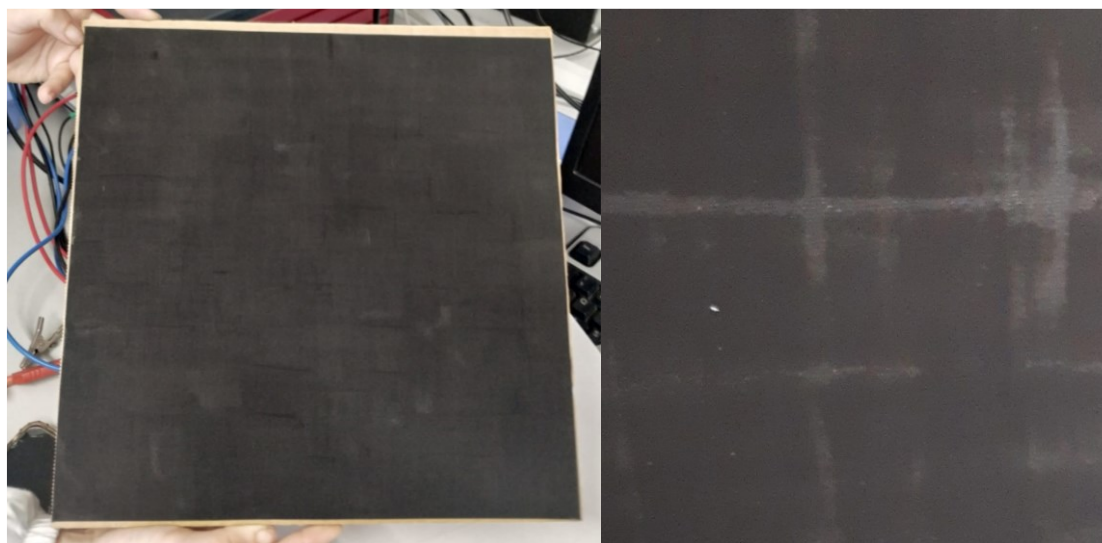


Figure B.26 - Commercial electrode used with $0.5 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 % (30 cm x 30 cm).

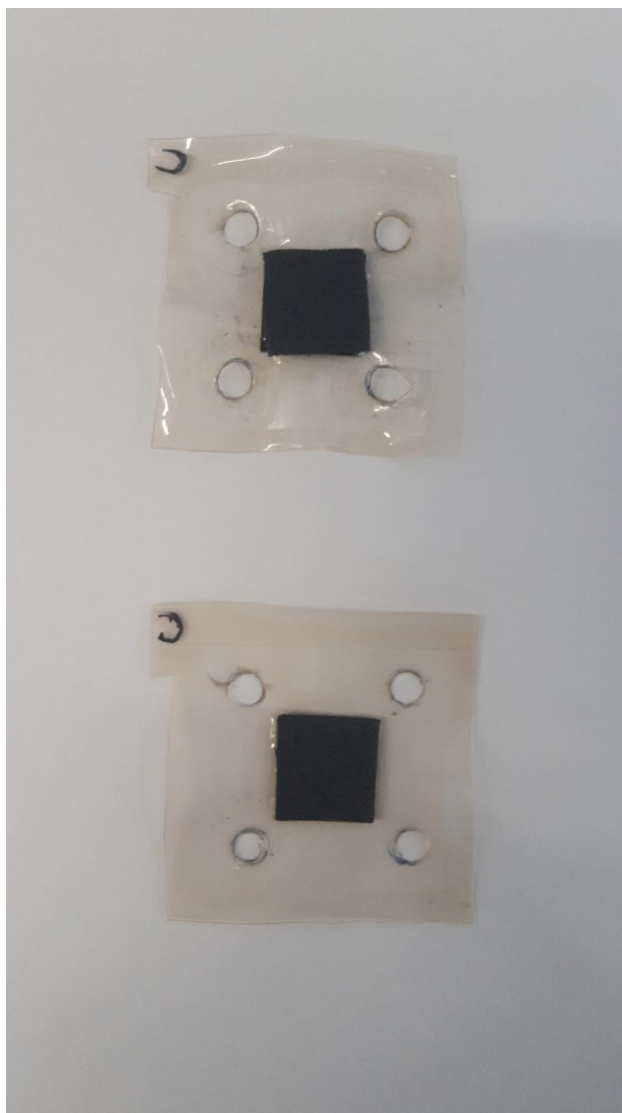


Figure B.27 - MEA not pressed (above) and MEA pressed (below).

B.2.1 SEM analysis

The SEM/EDS analysis was performed using a High resolution (Schottky) Environmental Scanning Electron Microscope with X-Ray Microanalysis and Electron Backscattered Diffraction analysis: FEI Quanta 400 FEG ESEM / EDAX Genesis X4M.

The analysis was performed on a commercial and “handmade” electrode with a loading of $0.5 \text{ mg} \cdot \text{cm}^{-2}$ Pt/C 60 %. The “Amostra 2” stands for a commercial electrode and the “Amostra 3” e “Amostra 4” for a “handmade” electrode before and after being tested in the cell, respectively. The Z_1 , Z_2 and Z_3 are different places in the electrode samples with different proportions of platinum and the brighter one represents points where there is less carbon, i.e., more platinum because the platinum is the metal with higher atomic number, so in the electron backscattered diffraction method is represented by the brighter points.

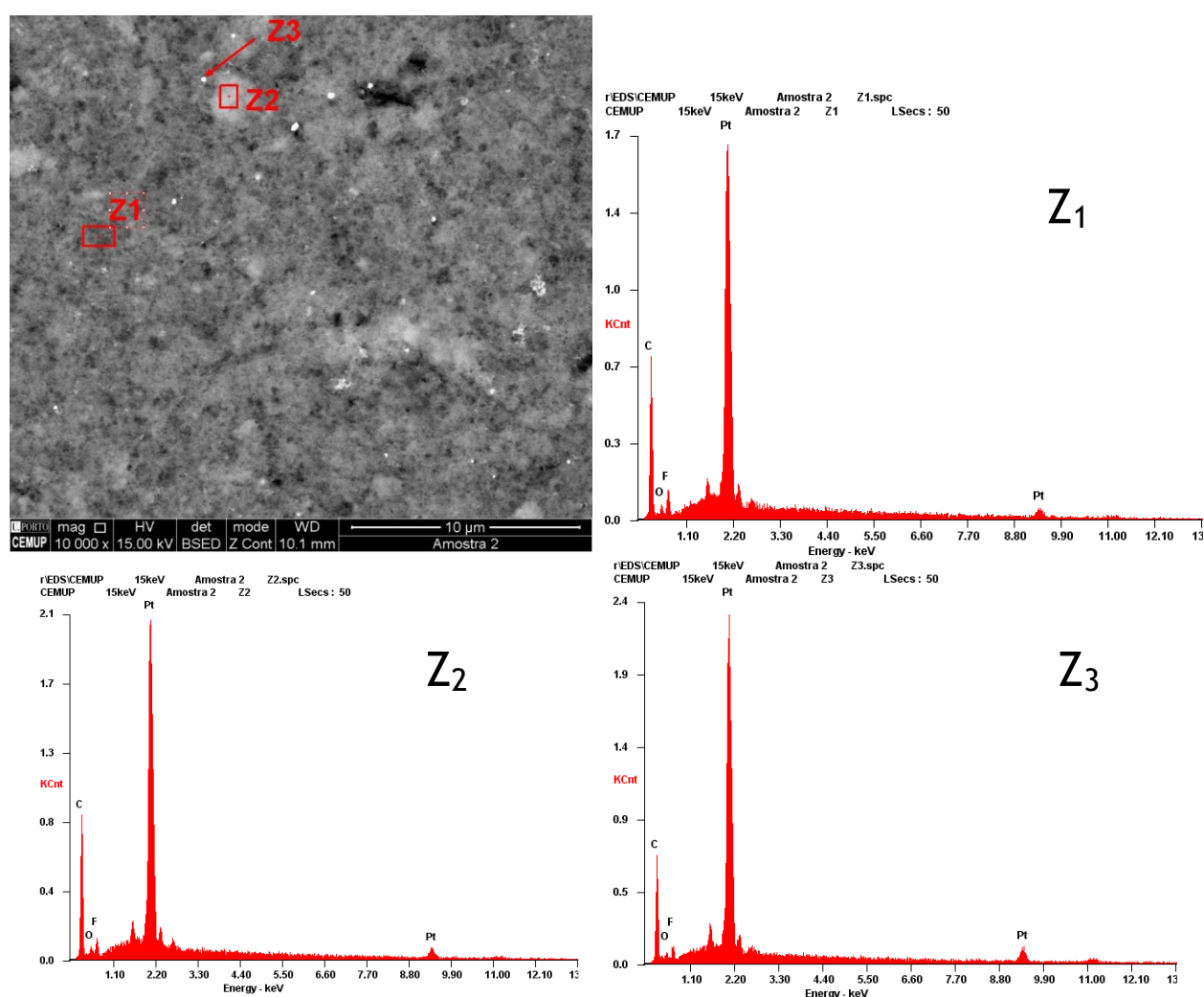


Figure B.28 - SEM Analysis of a commercial electrode of $0.5 \text{ mg} \cdot \text{cm}^{-2}$ Pt/C 60 %.

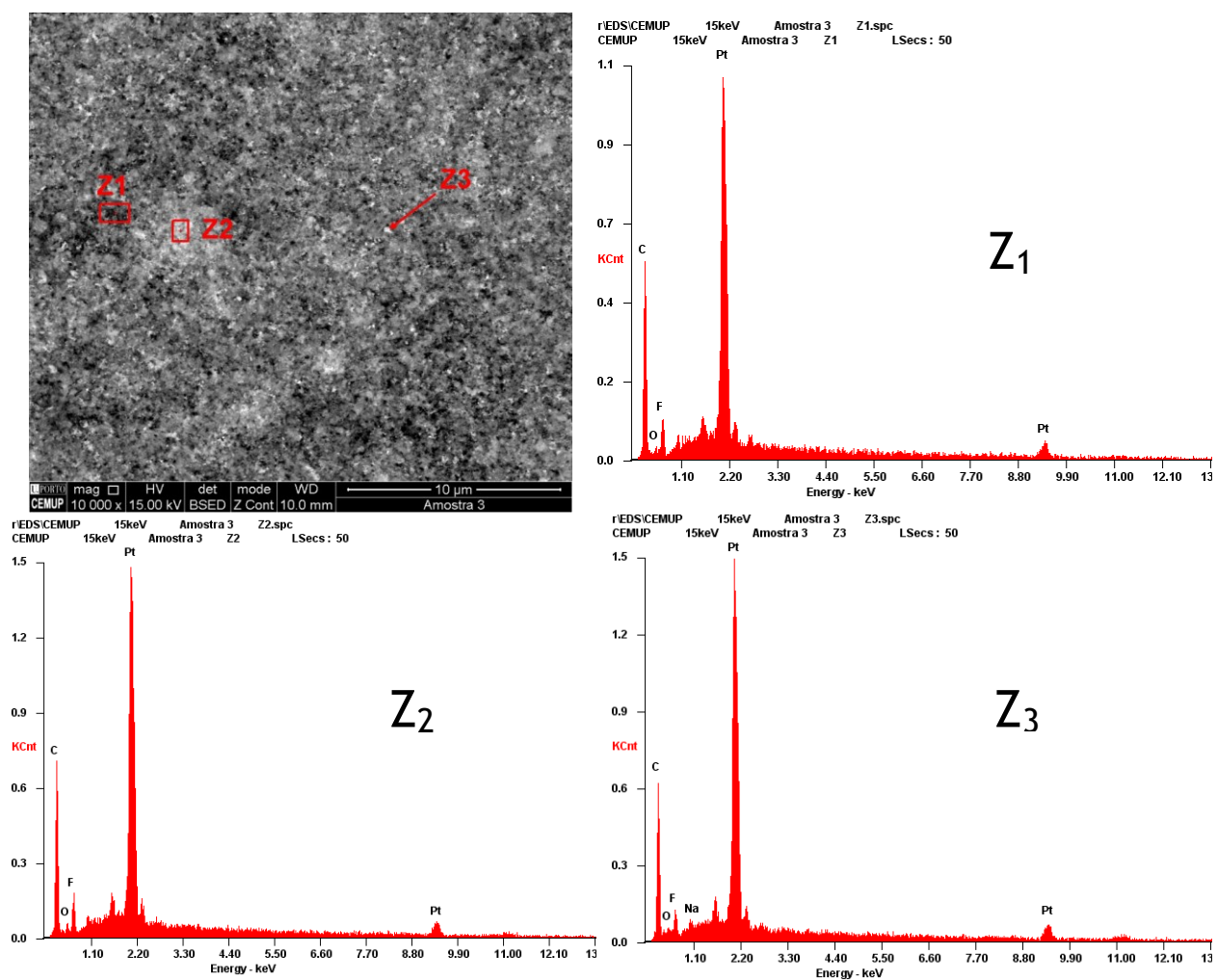


Figure B.29 - SEM Analysis of a electrode prepared in LSRE-LCM of $0.5 \text{ mg} \cdot \text{cm}^{-2}$ Pt/C 60 %.

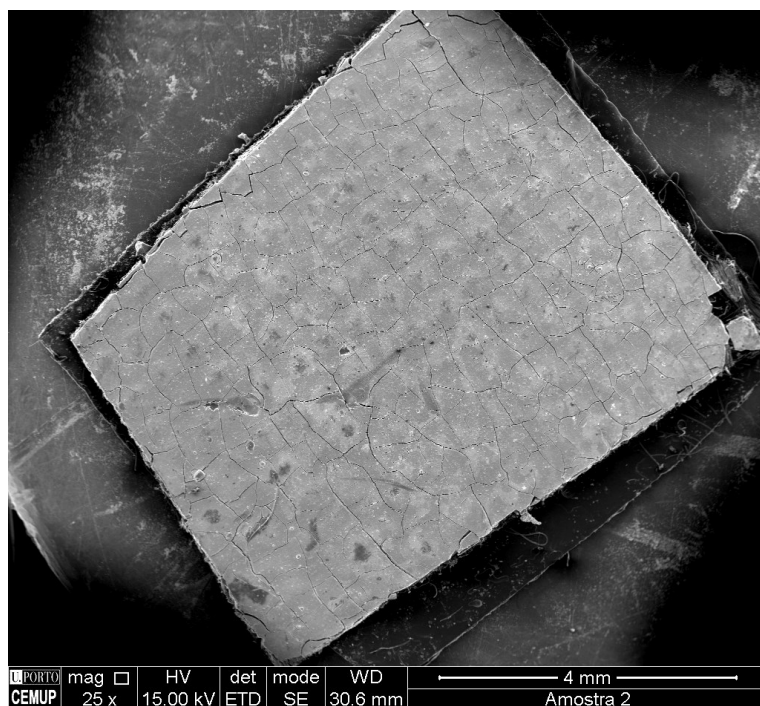


Figure B.30 - Global vision of “Amostra 2”

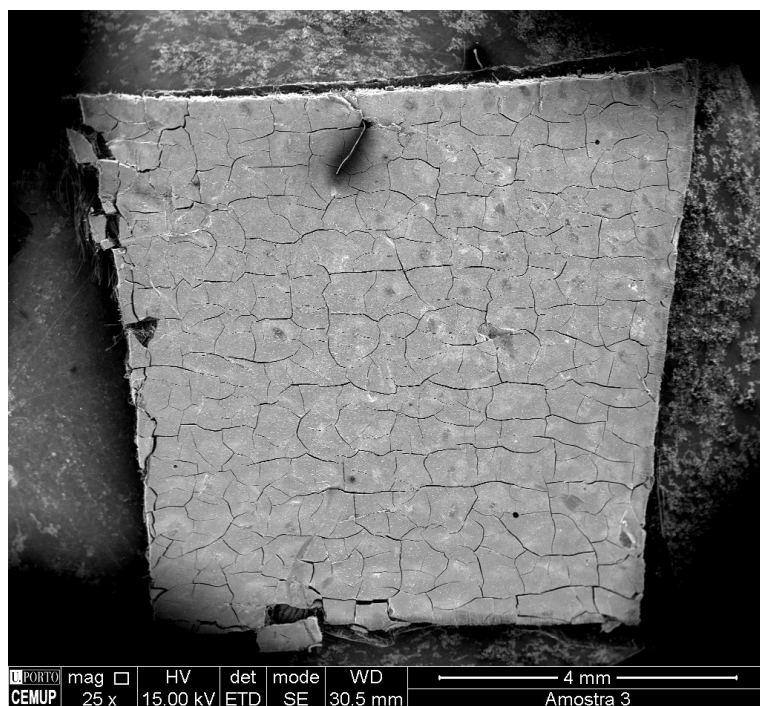


Figure B.31 - Global vision of “Amostra 3”

Observing Figure B.30 and B.31 is possible to affirm that is not visible many differences when looking at the global vision of the electrode prepared in laboratory and the commercial one.

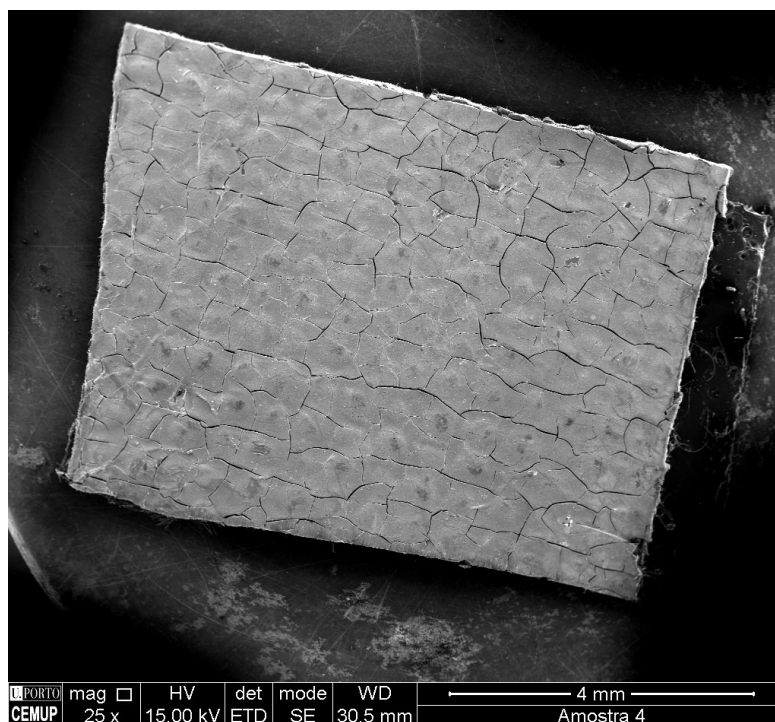


Figure B.32 - Global vision of “Amostra 4”

The “Amostra 4” represents the electrode after being teste in the mpDMFC. As is not visible differences in relation to the electrode before being tested in the cell, it can be concluded that was not visible a degradation of the catalyst.

B.3 Effect of cathode catalyst properties

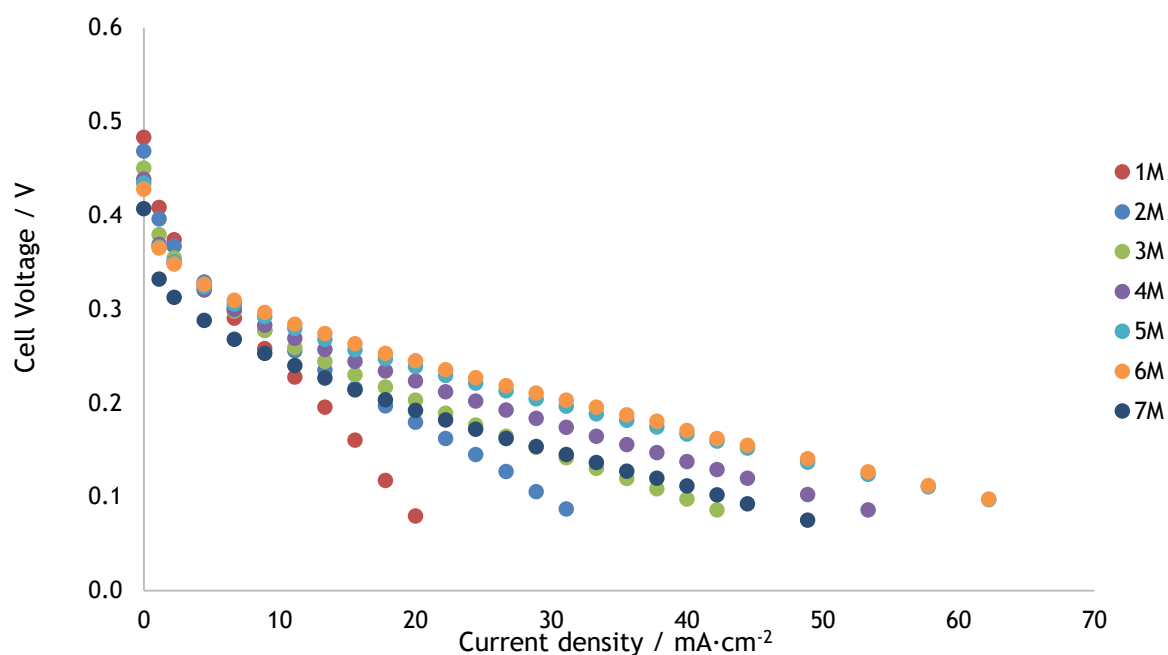


Figure B.33 - Effect of the methanol concentration on the cell performance for a cathode catalyst load of $2 \text{ mg} \cdot \text{cm}^{-2} \text{ Pt/C } 60 \%$.

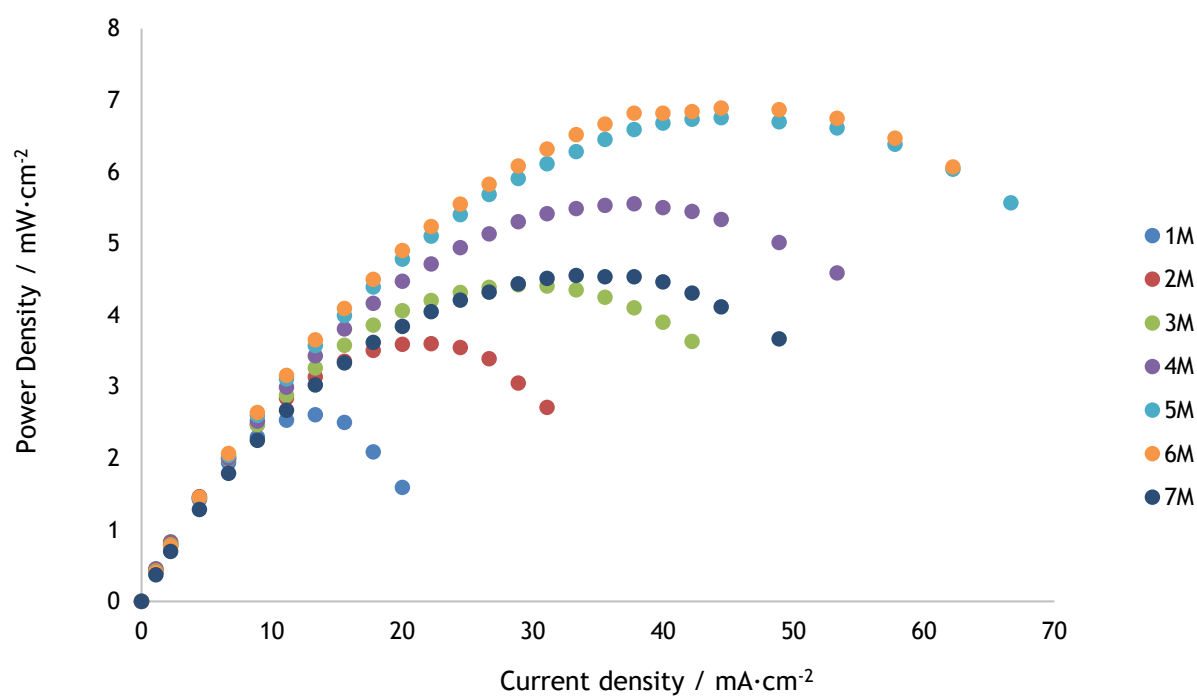


Figure B.34 - Effect of the methanol concentration on the cell power density for a cathode catalyst load of $2 \text{ mg} \cdot \text{cm}^{-2} \text{ Pt/C } 60 \%$.

Table B.5 - Resistance values and maximum power density for a cathode catalyst load of $2 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 %.

Concentration / M	Voltage/ V	R_{Ω}	R_1	R_2	Maximum power density / $\text{mW}\cdot\text{cm}^{-2}$
1	0.20	0.50	2.1	3.2	2.7
	0.30	0.50	2.3	5.1	
	0.40	0.51	3.0	13	
2	0.20	0.48	1.4	2.0	3.6
	0.30	0.49	1.4	4.1	
	0.40	0.49	1.8	15	
3	0.20	0.51	0.97	1.5	4.4
	0.30	0.50	1.0	3.9	
	0.40	0.50	1.1	18	
4	0.20	0.52	0.69	1.2	5.6
	0.30	0.53	0.86	3.5	
	0.40	0.53	1.0	19	
5	0.20	0.44	0.52	0.93	6.8
	0.30	0.45	0.65	2.8	
	0.40	0.45	0.81	19	
6	0.20	0.52	0.48	0.94	6.9
	0.30	0.53	0.52	3.1	
	0.40	0.53	0.73	19	
7	0.20	0.53	0.66	1.7	4.6
	0.30	0.53	0.86	7.9	
	0.40	0.54	1.1	16	

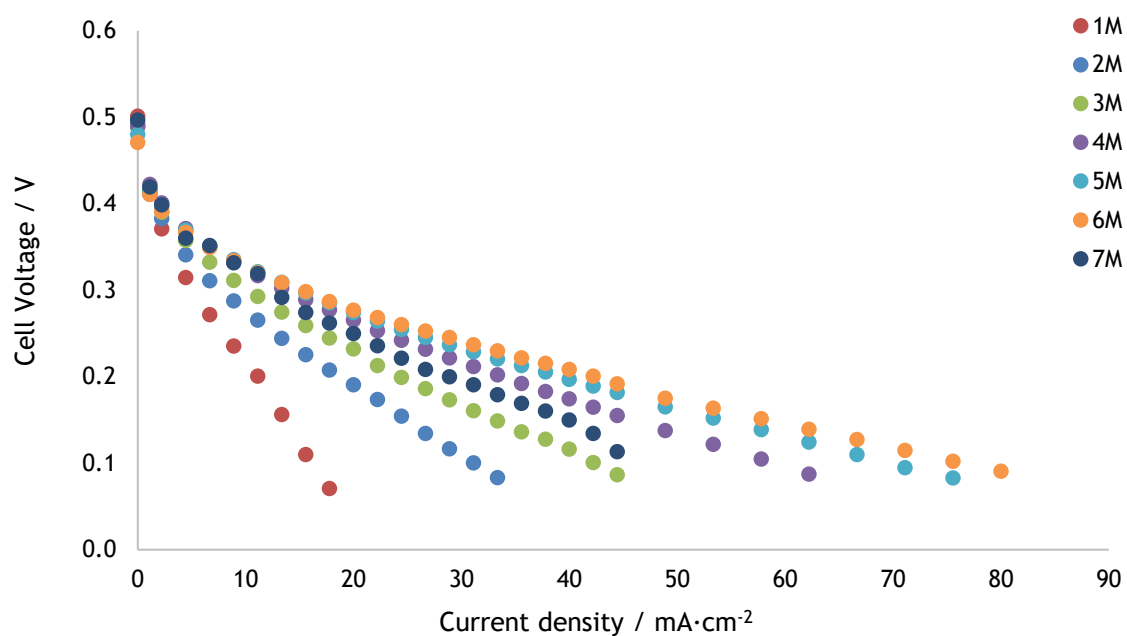


Figure B.35 - Effect of the methanol concentration on the cell performance for a cathode catalyst load of $4 \text{ mg} \cdot \text{cm}^{-2} \text{ Pt/C } 60 \%$.

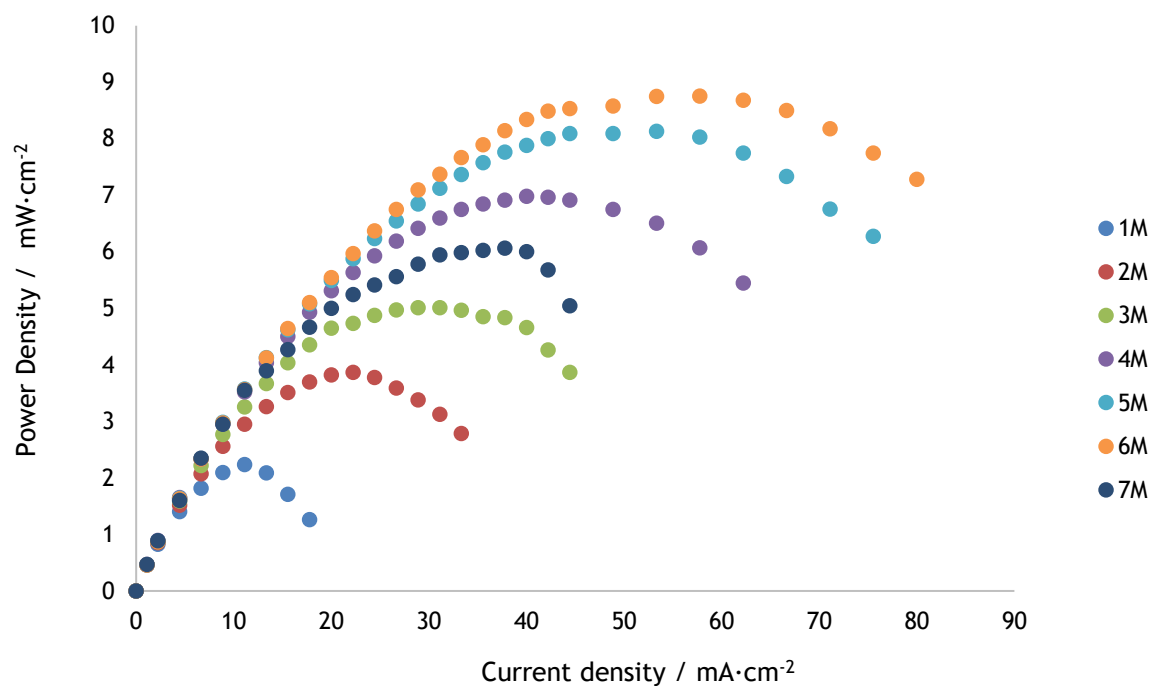


Figure B.36 - Effect of the methanol concentration on the cell power density for a cathode catalyst load of $4 \text{ mg} \cdot \text{cm}^{-2} \text{ Pt/C } 60 \%$.

Table B.6 - Resistance values and maximum power density for a cathode catalyst load of $4 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 60 %.

Concentration / M	Potential / V	R_0	R_1	R_2	Maximum power density / $\text{mW}\cdot\text{cm}^{-2}$
1	0.20	0.48	2.0	4.5	2.2
	0.30	0.48	2.7	6.7	
	0.40	0.48	4.7	14	
2	0.20	0.43	1.0	2.4	3.9
	0.30	0.44	1.7	3.5	
	0.40	0.43	2.2	12	
3	0.20	0.42	1.1	1.2	5.0
	0.30	0.42	1.4	2.4	
	0.40	0.43	1.5	12	
4	0.20	0.43	0.67	0.96	7.0
	0.30	0.43	1.0	1.8	
	0.40	0.44	1.1	10	
5	0.20	0.47	0.67	0.86	8.1
	0.30	0.48	0.95	1.8	
	0.40	0.37	0.98	12	
6	0.20	0.35	0.65	0.69	8.8
	0.30	0.35	0.68	1.9	
	0.40	0.33	0.80	15	
7	0.20	0.31	0.51	0.83	6.1
	0.30	0.27	0.59	1.6	
	0.40	0.27	0.88	9.7	

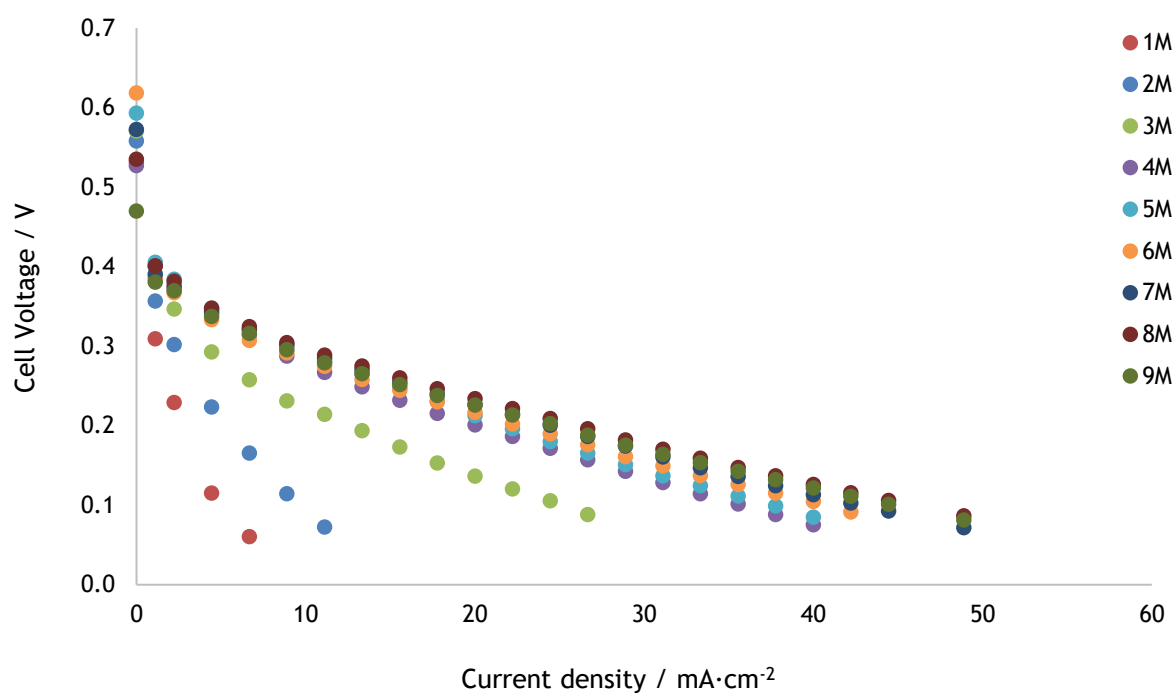


Figure B.37 - Effect of the methanol concentration on the cell performance for a cathode catalyst load of $2\text{ mg}\cdot\text{cm}^{-2}$ Pt/C 40 %.

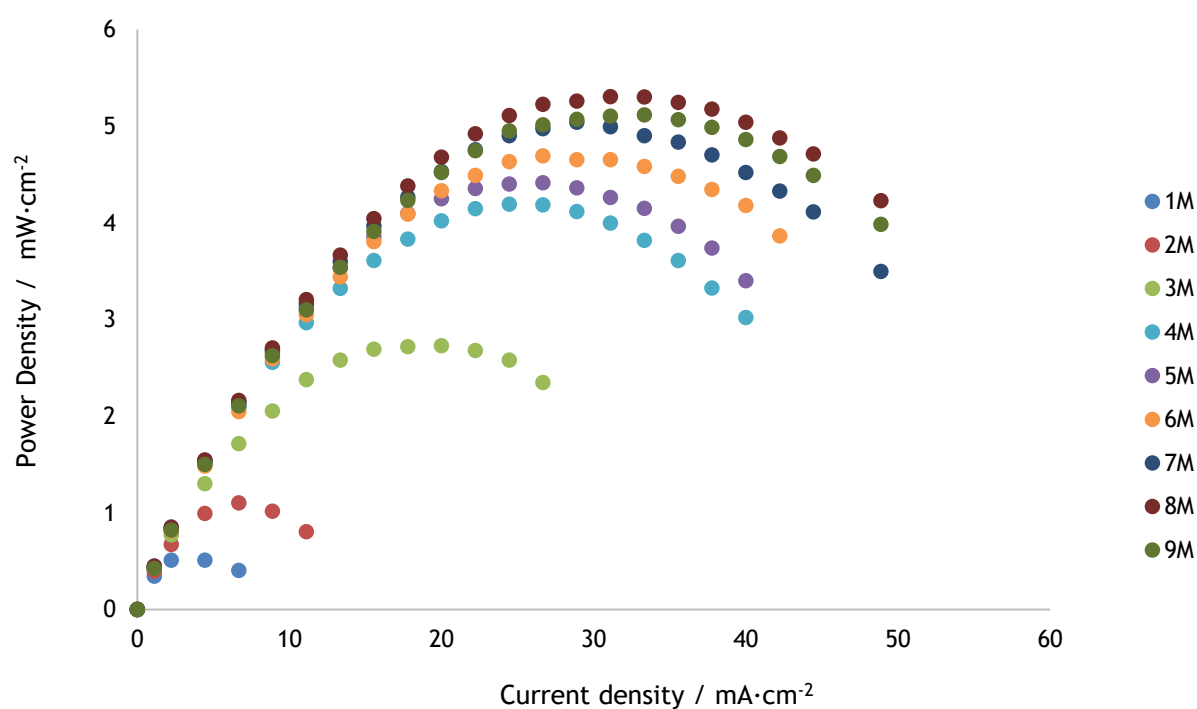


Figure B.38 - Effect of the methanol concentration on the cell power density for a cathode catalyst load of $2\text{ mg}\cdot\text{cm}^{-2}$ Pt/C 40 %.

Table B.7 - Resistance values and maximum power density for a cathode catalyst load of $2 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 40 %.

Concentration / M	Voltage/ V	R_0	R_1	R_2	Maximum power density / $\text{mW}\cdot\text{cm}^{-2}$
1	0.20	0.40	11	13	0.5
	0.30	0.38	16	20	
	0.40	0.38	23	34	
2	0.20	0.57	7.3	6.3	1.1
	0.30	0.65	9.6	11	
	0.40	0.56	14	25	
3	0.20	0.34	2.7	1.3	2.7
	0.30	0.34	4.0	3.6	
	0.40	0.34	6.1	18	
4	0.20	0.40	1.9	1.4	4.2
	0.30	0.40	3.0	3.3	
	0.40	0.41	3.5	20	
5	0.20	0.38	1.6	1.4	4.4
	0.30	0.38	1.7	3.2	
	0.40	0.38	2.2	18	
6	0.20	0.37	1.2	1.5	4.7
	0.30	0.33	1.5	3.3	
	0.40	0.33	1.9	22	
7	0.20	0.56	1.1	1.5	5.0
	0.30	0.56	1.3	3.7	
	0.40	0.36	1.5	23	
8	0.20	0.39	0.85	1.6	5.3
	0.30	0.40	1.0	4.0	
	0.40	0.38	1.3	23	
9	0.20	0.36	0.78	1.7	5.1
	0.30	0.37	0.96	4.8	
	0.40	0.37	1.3	24	

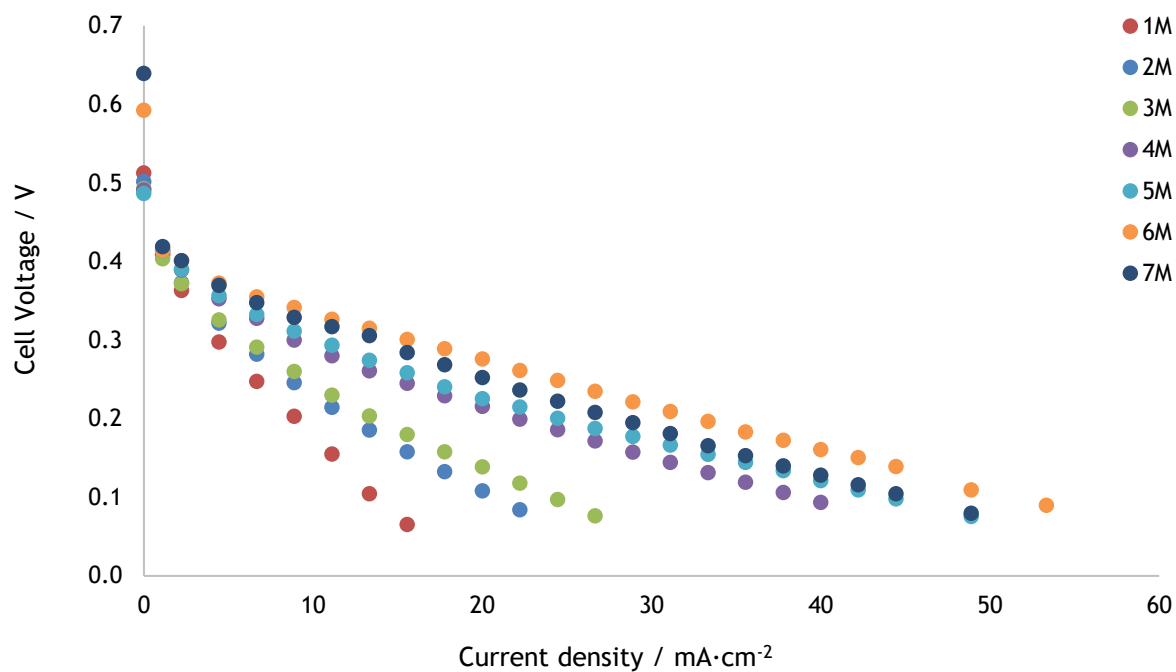


Figure B.39 - Effect of the methanol concentration on the cell performance for a cathode catalyst load of 4 mg·cm⁻² Pt/C 40 %.

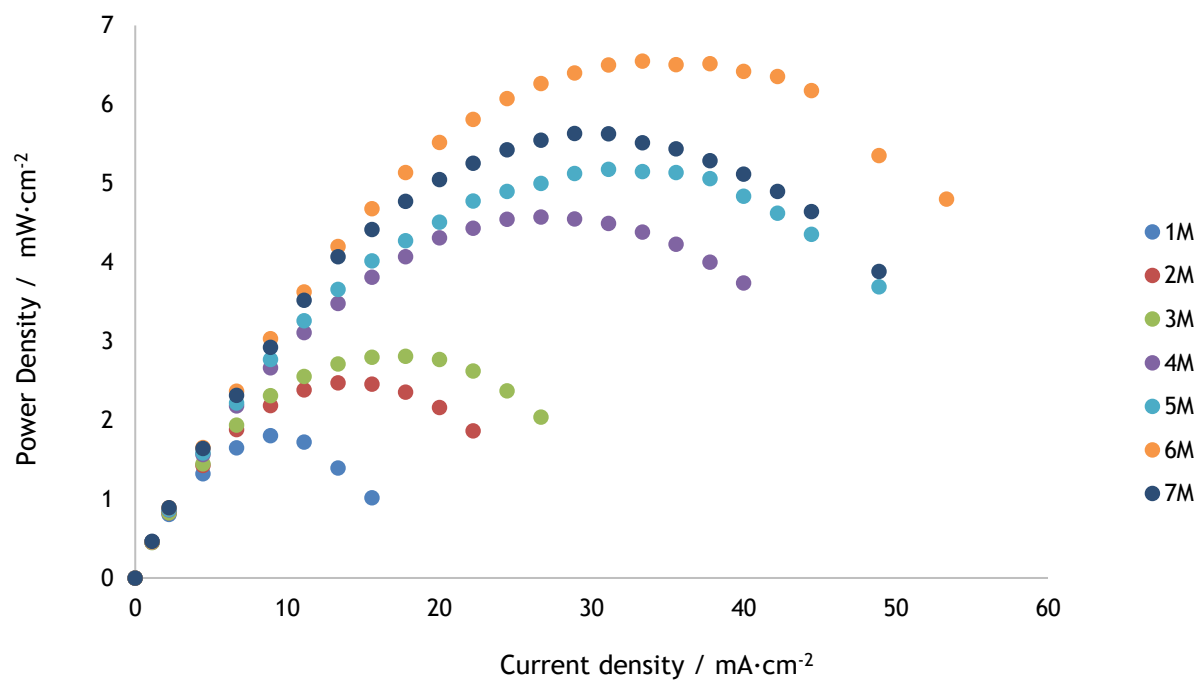


Figure B.40 - Effect of the methanol concentration on the cell power density for a cathode catalyst load of 4 mg·cm⁻² Pt/C 40 %.

Table B.8 - Resistance values and maximum power density for a cathode catalyst load of $4 \text{ mg}\cdot\text{cm}^{-2}$ Pt/C 40 %.

Concentration / M	Voltage/ V	R_0	R_1	R_2	Maximum power density / $\text{mW}\cdot\text{cm}^{-2}$
1	0.20	0.49	2.1	5.9	1.8
	0.30	0.48	2.5	10	
	0.40	0.48	2.6	18	
2	0.20	0.50	1.9	3.7	2.5
	0.30	0.48	2.6	5.7	
	0.40	0.47	3.8	14	
3	0.20	0.48	1.6	2.4	2.8
	0.30	0.49	2.7	4.0	
	0.40	0.50	2.9	15	
4	0.20	0.48	1.3	1.7	4.6
	0.30	0.48	1.7	3.2	
	0.40	0.48	2.0	13	
5	0.20	0.46	1.0	1.4	5.2
	0.30	0.47	1.5	2.7	
	0.40	0.47	1.8	14	
6	0.20	0.46	0.71	1.3	6.6
	0.30	0.48	0.78	2.1	
	0.40	0.39	1.1	9.9	
7	0.20	0.36	0.45	1.7	5.7
	0.30	0.37	0.70	3.0	
	0.40	0.35	0.87	12	

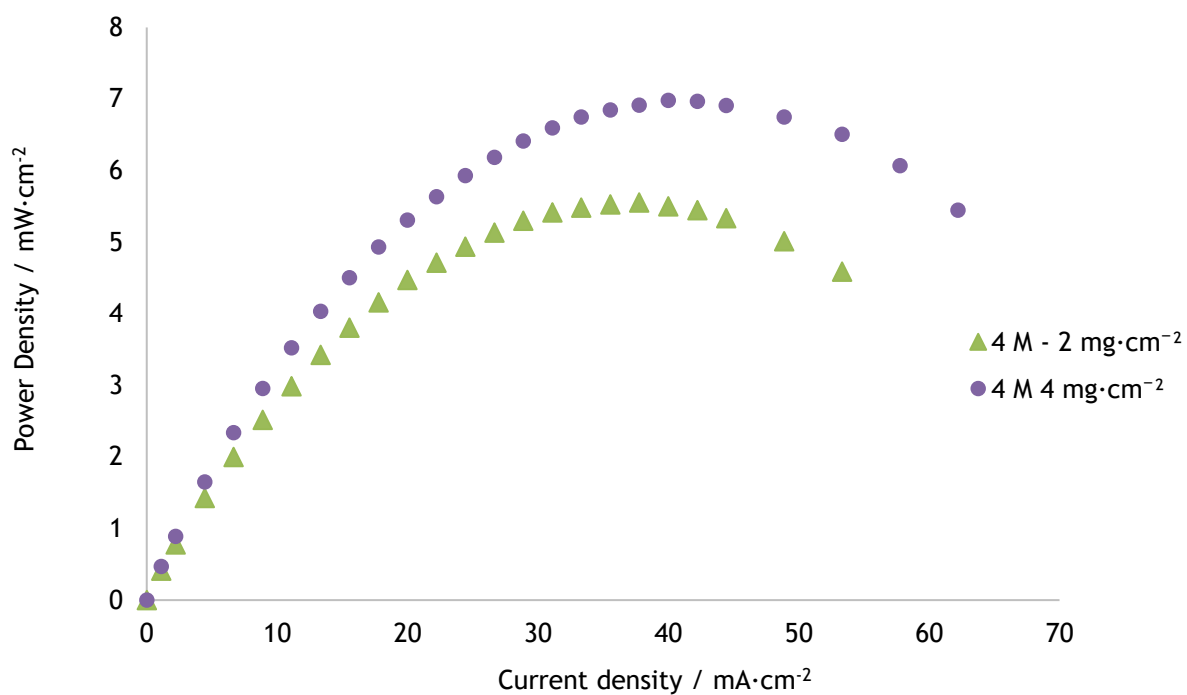


Figure B.41 - Effect of the catalyst load on the cell power density for a Pt/C 60 % catalyst.

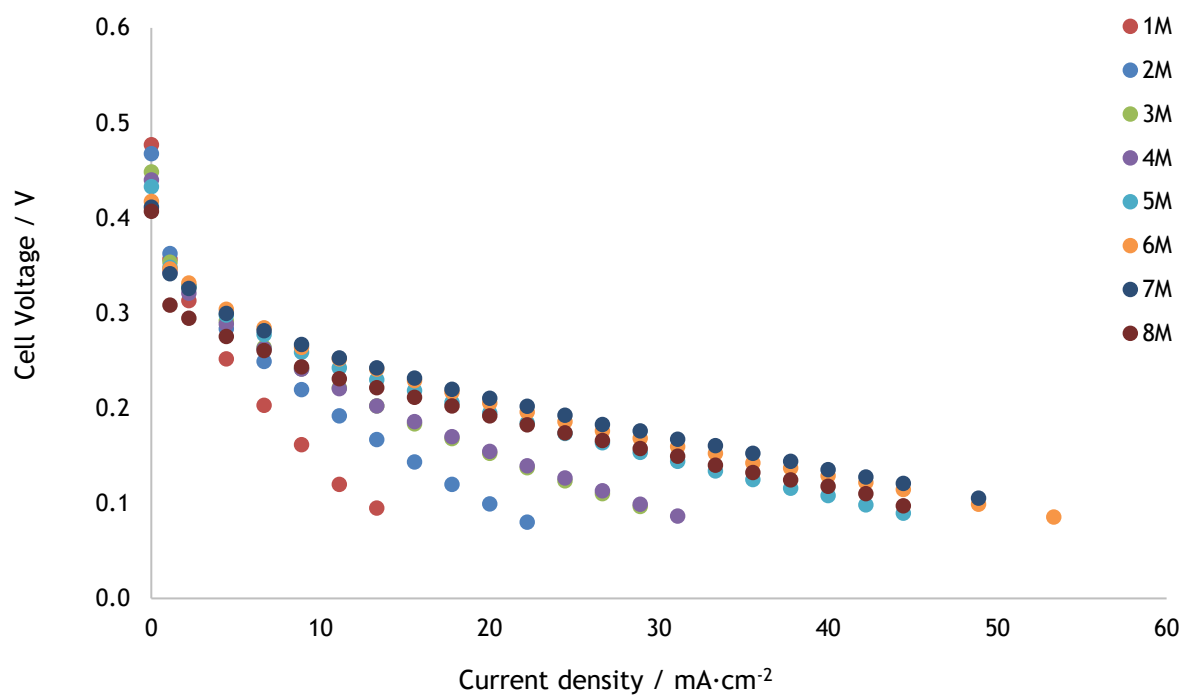


Figure B.42 - Effect of the methanol concentration on the cell performance for a cathode catalyst load of $2\text{ mg}\cdot\text{cm}^{-2}$ PtB.

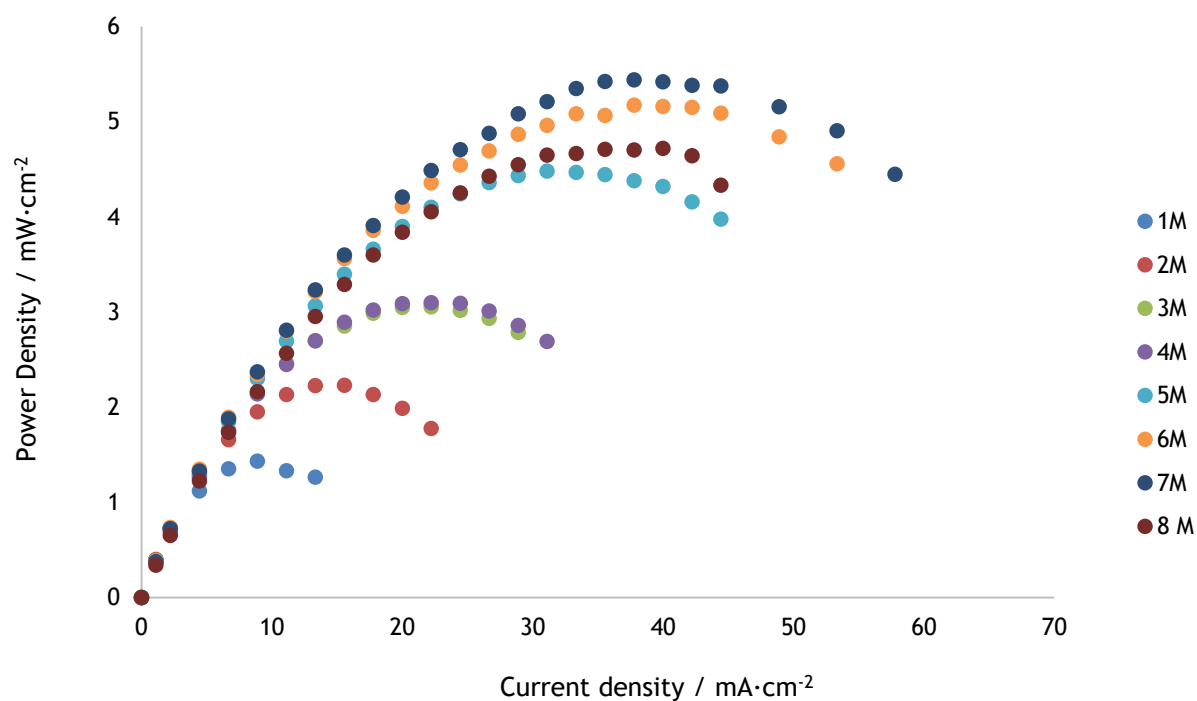


Figure B.43 - Effect of the methanol concentration on the cell power density for a cathode catalyst load of $2\text{ mg}\cdot\text{cm}^{-2}$ PtB.

Table B.9 - Resistance values and maximum power density for a cathode catalyst load of $2 \text{ mg}\cdot\text{cm}^{-2}$ PtB.

Concentration / M	Voltage / V	R_{Ω}	R_1		R_2	Maximum power density / $\text{mW}\cdot\text{cm}^{-2}$
1	0.20	0.59	3.1		5.3	1.4
	0.30	0.59	3.9		9.7	
	0.40	0.62	4.3		28	
2	0.20	0.72	1.9		2.9	2.2
	0.30	0.86	2.5		7.0	
	0.40	0.48	3.1		27	
3	0.20	0.45	1.3		2.1	3.1
	0.30	0.46	1.9		5.9	
	0.40	0.46	2.3		24	
4	0.20	0.46	1.2		2.1	3.1
	0.30	0.47	1.7		7.4	
	0.40	0.46	2.6		21	
5	0.20	0.44	0.82		1.5	4.5
	0.30	0.44	1.1		5.7	
	0.40	0.45	1.5		22	
6	0.20	0.46	0.65		1.4	5.2
	0.30	0.47	0.94		4.7	
	0.40	0.48	1.4		23	
7	0.20	0.39	0.63		1.5	5.4
	0.30	0.40	1.0		6.9	
	0.40	0.40	1.4		22	
8	0.20	0.46	0.64		1.8	4.7
	0.30	0.46	0.91		7.9	
	0.40	0.45	1.2		22	

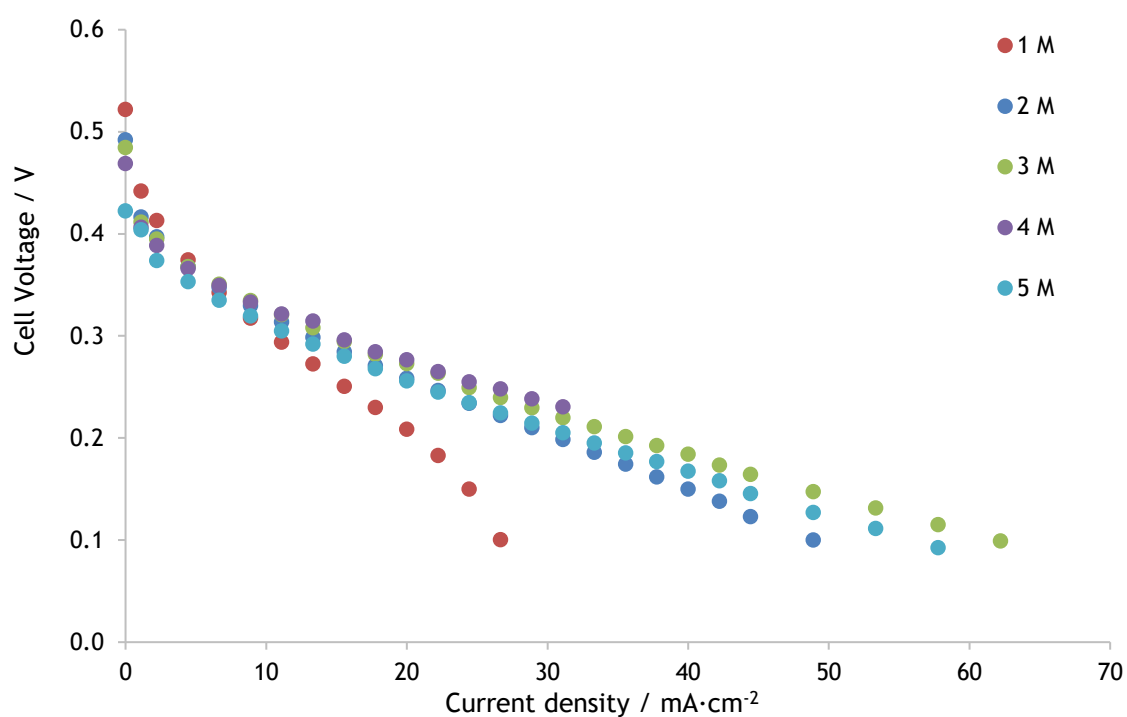


Figure B.44 - Effect of the methanol concentration on the cell performance for a cathode catalyst load of $4 \text{ mg}\cdot\text{cm}^{-2}$ PtB.

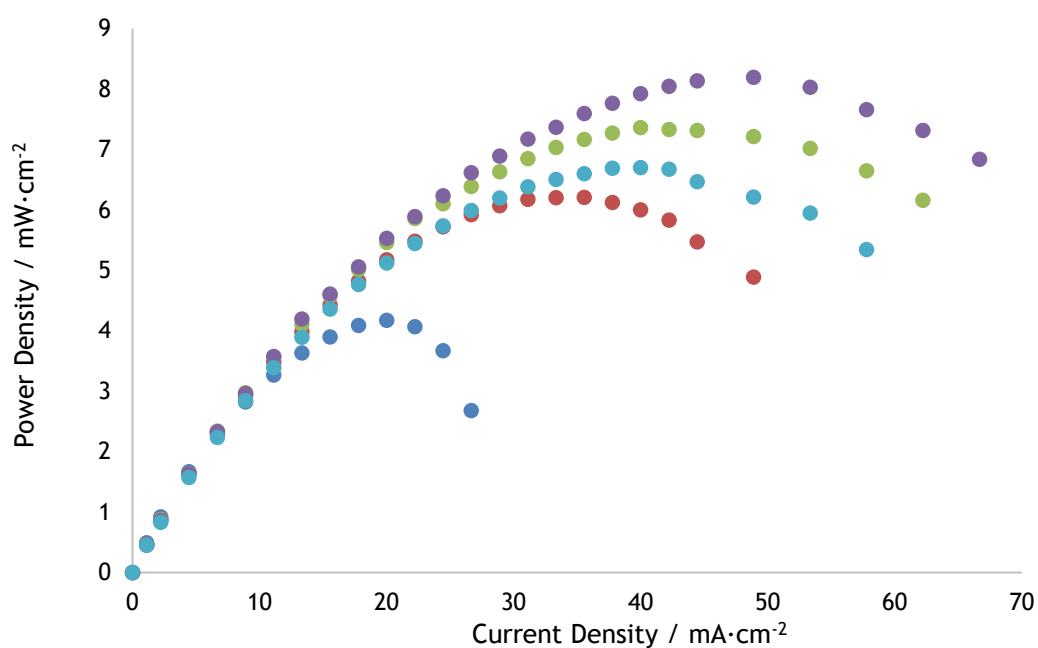


Figure B.45 - Effect of the methanol concentration on the cell power density for a cathode catalyst load of $4 \text{ mg}\cdot\text{cm}^{-2}$ PtB.

Table B.10 - Resistance values and maximum power density for a cathode catalyst load of $4 \text{ mg} \cdot \text{cm}^{-2} \text{ PtB}$.

Concentration / M	Voltage / V	R_{Ω}	R_1	R_2	Maximum power density / $\text{mW} \cdot \text{cm}^{-2}$
1	0.20	0.49	1.6	2.1	3.7
	0.30	0.49	1.7	3.2	
	0.40	0.47	1.9	8.3	
2	0.20	0.45	1.0	1.1	6.2
	0.30	0.46	1.1	1.9	
	0.40	0.46	1.2	8.8	
3	0.20	0.49	0.63	0.87	7.4
	0.30	0.49	0.78	1.8	
	0.40	0.50	0.94	11	
4	0.20	0.44	0.51	0.79	8.1
	0.30	0.45	0.62	1.9	
	0.40	0.45	0.75	15	
5	0.20	0.40	0.46	0.69	6.7
	0.30	0.41	0.57	1.8	
	0.40	0.41	0.76	16	

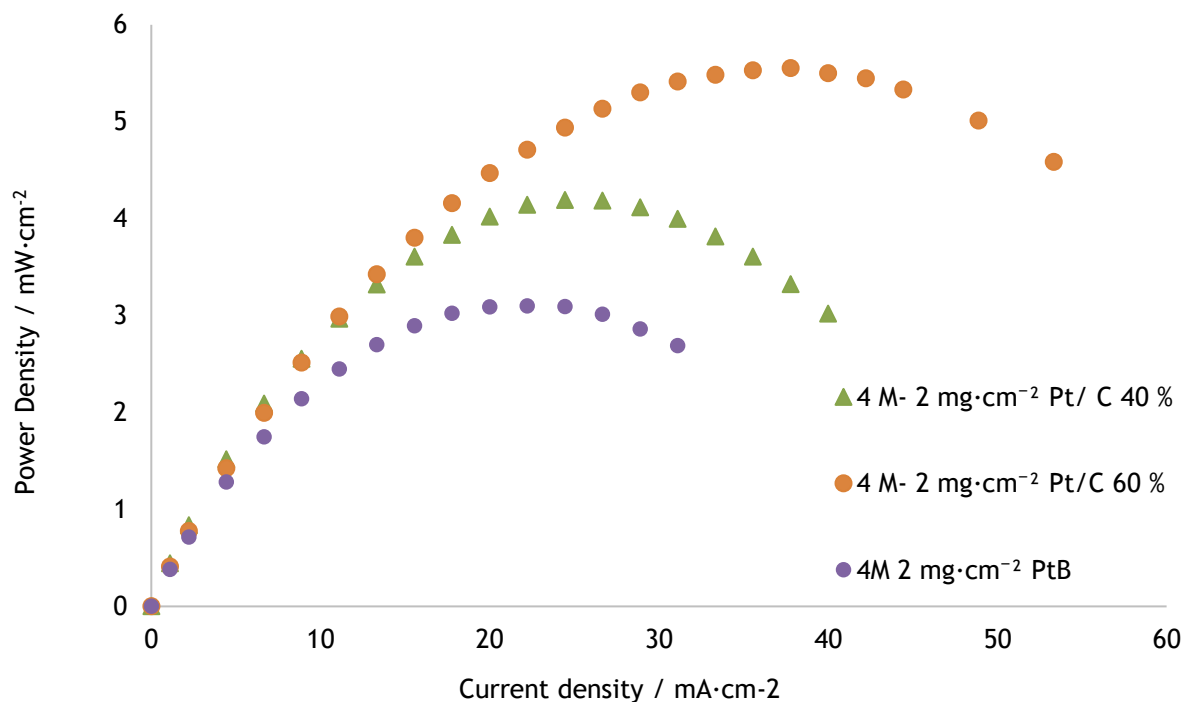


Figure B.46 - Effect of the catalyst support on the cell power density for a catalyst load of $2 \text{ mg}\cdot\text{cm}^{-2}$ Pt.

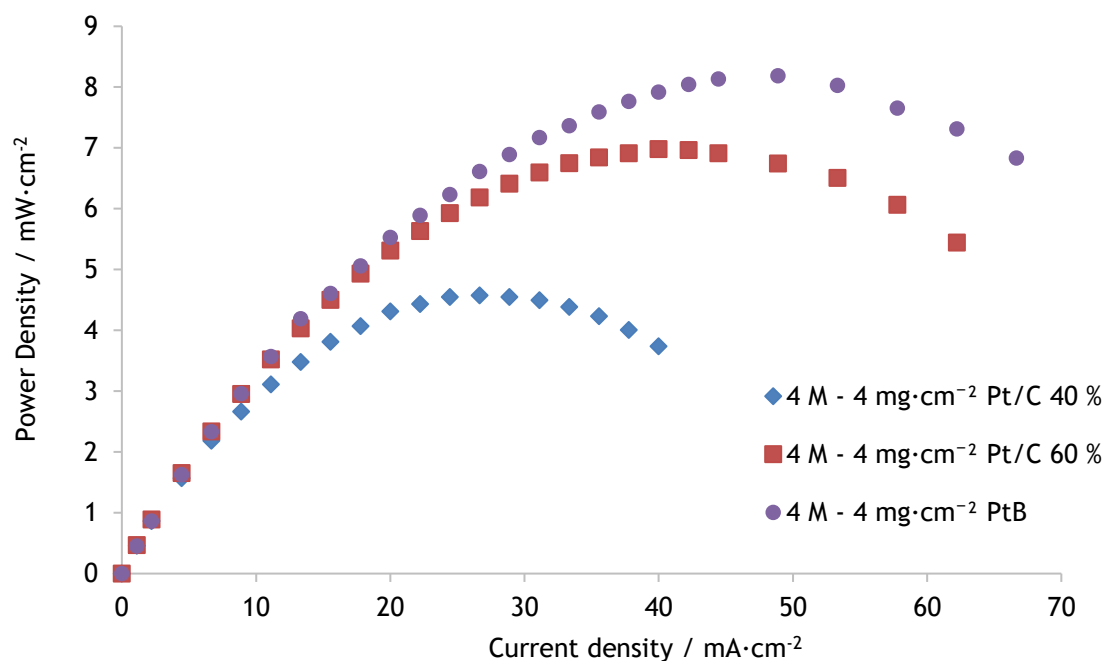


Figure B.47 - Effect of the catalyst support on the cell power density for a catalyst load of $4 \text{ mg}\cdot\text{cm}^{-2}$ Pt.

B.4 Effect of methanol concentration

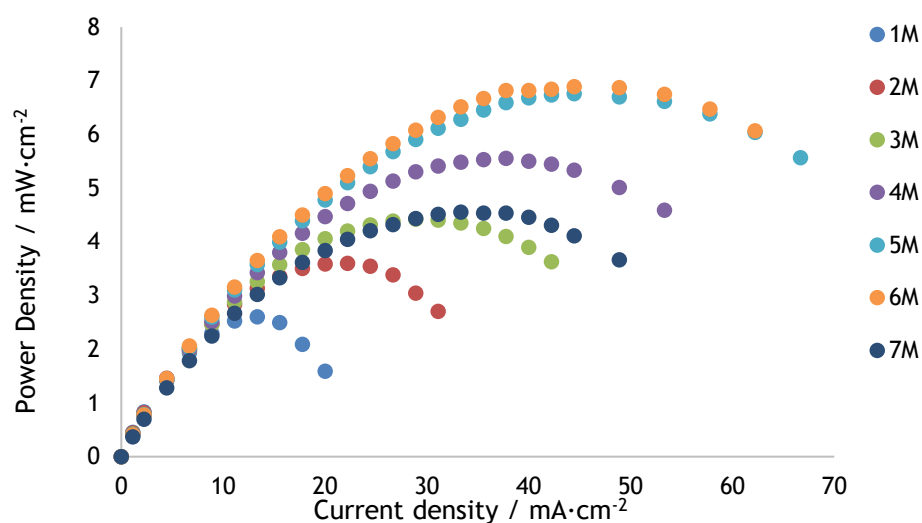


Figure B.48 - Effect of the methanol concentration on the cell power density.

Table B.11 - Resistance values and maximum power density for the study of methanol concentration.

Concentration / M	Voltage / V	R_0	R_1	R_2	Maximum power density / mW·cm ⁻²
1	0.20	0.50	2.1	3.2	2.7
	0.30	0.50	2.3	5.1	
	0.40	0.51	3.0	13	
3	0.20	0.51	0.97	1.5	4.4
	0.30	0.50	1.0	3.9	
	0.40	0.50	1.1	18	
4	0.20	0.52	0.7	1.2	5.6
	0.30	0.53	0.9	3.5	
	0.40	0.53	1.0	19	
5	0.20	0.44	0.52	0.93	6.8
	0.30	0.45	0.65	2.8	
	0.40	0.45	0.81	19	
7	0.20	0.53	0.66	1.7	4.6
	0.30	0.53	0.86	7.8	
	0.40	0.54	1.1	16	



Figure B.49 - Visualization of the CO₂ bubbles at the anode side.

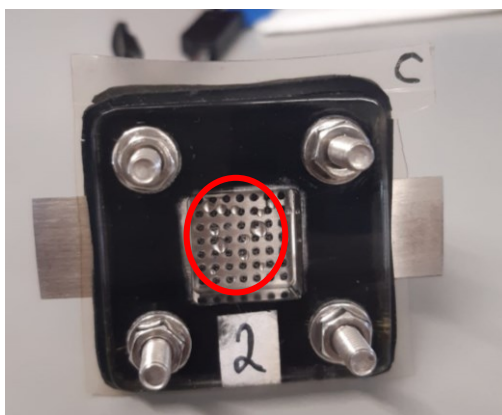


Figure B.50 - Visualization of the water droplets at the cathode side.

B.4 Main results

Table B.12 - Summary of the results obtained for the different conditions studied.

Assay	MEA	Electrodes		Methanol concentration / M	Maximum Power Density / mW·cm ⁻²
		Anode	Cathode		
1	Not pressed	3.0 mg·cm ⁻² Pt-Ru commercial	0.50 mg·cm ⁻² Pt/C 60 % commercial	7.0	0.8
2	Pressed		0.50 mg·cm ⁻² Pt/C 60 % commercial	7.0	1.8
3	Not pressed		0.44 mg·cm ⁻² Pt/C 60 %	9.0	1.1
4	Pressed		0.50 mg·cm ⁻² Pt/C 60 %	6.0	1.4
5			1.7 mg·cm ⁻² Pt/C 60 %	6.0	6.9
6			4.1 mg·cm ⁻² Pt/C 60 %	6.0	8.8
7			1.9 mg·cm ⁻² Pt/C 40 %	8.0	5.3
8			4.0 g·cm ⁻² Pt/C 40 %	6.0	6.6
9			1.7 mg·cm ⁻² PtB	7.0	5.4
10			3.7 mg·cm ⁻² PtB	4.0	8.1

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