

Master in Chemical Engineering

***Laser Structured Gas Diffusion Layers in PEM
Fuel Cells - a study on the hydrophobicity and
wettability***

A Master's dissertation

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DLR

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Abstract

Proton exchange membrane fuel cells continue to receive great attention due to its promising characteristics as technologies for clean energy applications. Despite the continuous efforts to make this technology commercially available, its design faces a major challenge, the water management, especially at the cathode side. The delicate balance required for maintaining a good humidification of the proton exchange membrane, while effectively removing water away from the catalyst layer, has a great impact on the performance of these fuel cells and should not be compromised.

The gas diffusion layer, composed by a macro and a micro porous layer coated above it, plays an important role in the water management phenomenon, since both humidification and water removal are achieved through this porous structure. It is important, therefore, to proper measure its main properties, such as the wettability of the inner surfaces.

This work had the main goal of adding some understanding to the role of the gas diffusion layer in the overall performance of the proton exchange membrane fuel cells, when it is applied a laser treatment to the micro porous layer side. Laser parameters such as pattern, output power and speed were optimized and applied in this technique. *Ex-situ* and *in-situ* methods, like EDX measurements and polarization curves at different relative humidity conditions were investigated. Furthermore, the wettability of the modified structures was analyzed through the Washburn method and the Owens-Wendt two-parameter model, towards the extrapolation of contact angles between the different gas diffusion layers and water.

The results showed an improvement of the performance of the fuel cell when assembled with a laser modified gas diffusion layer, at laser process speed of $1 \text{ mm}\cdot\text{s}^{-1}$ and laser output power of ca.250 mW, in the cathode side. In addition, it was observed an increase in the main functioning when both anode and cathode humidifiers worked at 75 % relative humidity conditions. The application of the Washburn method to study the wettability was proved to be insufficient to extrapolate the data, whereas when combining this method with the Owens-Wendt model, accurate results were obtained. However, the hydrophilic properties of the gas diffusion layers were not enhanced, as expected, leading to the need of further improvements. For instances, the development of models that take in consideration the data extrapolated in the scope of this work could help in the support and design of proton exchange membrane fuel cells, towards its commercial availability with reduced costs and with reduced water management issues.

Keywords: Proton exchange membrane fuel cells; Gas diffusion layer; Laser modification; Wettability; Washburn method; Owens-Wendt two-parameter model.

Resumo

As células de combustível com membrana de permuta protônica continuam a receber grande atenção devido às suas características promissoras como tecnologias para aplicações de energia limpa. Apesar dos esforços contínuos para tornar comercialmente viável esta tecnologia, o seu projeto enfrenta um grande desafio: a gestão da água, especialmente no lado do cátodo. O equilíbrio necessário para manter uma boa humidificação da membrana, ao mesmo tempo que se remove, efetivamente, a água da camada catalítica, tem um grande impacto no desempenho destas células e não deve ser comprometido. A camada de difusão gasosa, composta por uma macro e uma micro camada porosa, desempenha um papel importante no fenómeno da gestão da água, uma vez que tanto a humidificação como a remoção da água são obtidas através desta estrutura porosa. É importante, portanto, caracterizar adequadamente suas principais propriedades, tais como a molhabilidade das superfícies internas.

Este trabalho tem como objetivo principal adicionar algum conhecimento sobre o papel da camada de difusão gasosa no desempenho global das células de combustível, quando é aplicado um tratamento a laser no lado da micro camada porosa. Alguns parâmetros relacionados com o laser, como o padrão, potência e velocidade, foram otimizados e aplicados nesta técnica. Métodos *ex-* e *in-situ*, como EDX e curvas de polarização a diferentes condições de humidade relativa, foram investigados. Além disso, a molhabilidade das estruturas modificadas foi analisada através do método de Washburn e do modelo a dois parâmetros de Owens-Wendt, com vista à extrapolação dos ângulos de contato entre as diferentes camadas de difusão gasosa e a água.

Os resultados evidenciaram melhorias no desempenho da célula quando uma camada de difusão gasosa modificada era colocada no lado do cátodo, com velocidade de processamento de $1 \text{ mm} \cdot \text{s}^{-1}$ e potência de, aproximadamente, 250 mW. Foi ainda observado um aumento no desempenho para uma humidificação de 75 %, do lado do ânodo e do cátodo. O método de Washburn, para o estudo da molhabilidade, mostrou-se insuficiente para a extrapolação dos dados, mas a combinação deste com o modelo de Owens-Wendt levou a uma maior precisão nos resultados. No entanto, as propriedades hidrofílicas das camadas não foram melhoradas, como esperado, levando à necessidade de futuros desenvolvimentos. Por exemplo, o uso de modelos que tenham em consideração os dados extrapolados neste trabalho poderia ajudar no projeto das células de combustível para a sua disponibilidade comercial, com custos e problemas de gestão da água reduzidos.

Palavras-chave: Células de combustível com membrana de permuta protônica; Camada de difusão gasosa; Molhabilidade; Método de Washburn; Modelo de Owens-Wendt.

Declaration

I hereby declare, on my word of honor, that this work is original and that all non-original contributions were properly referenced with source identification.

Beatriz Rebelo Pedrosa

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Notation and Glossary

v	Laser process speed	$\text{mm}\cdot\text{s}^{-1}$
m	Mass of liquid absorbed	g
t	Time	s
C_W	Washburn constant	

Greek Letters

μ	Dynamic viscosity	$\text{Pa}\cdot\text{s}^{-1}$
ρ	Density	$\text{kg}\cdot\text{m}^{-3}$
σ_{LV}^d	Dispersive component of the liquid/vapour surface tension	$\text{N}\cdot\text{m}^{-1}$
σ_{SV}^d	Dispersive component of the solid/vapour surface tension	$\text{N}\cdot\text{m}^{-1}$
$\sigma_{LV}^{\text{total}}$	Overall liquid/vapour surface tension	$\text{N}\cdot\text{m}^{-1}$
$\sigma_{SV}^{\text{total}}$	Overall solid/vapour surface tension	$\text{N}\cdot\text{m}^{-1}$
σ_{LV}^p	Polar component of the liquid/vapour surface tension	$\text{N}\cdot\text{m}^{-1}$
σ_{SV}^p	Polar component of the solid/vapour surface tension	$\text{N}\cdot\text{m}^{-1}$
θ	Internal contact angle	°
$\theta_{\text{H}_2\text{O}}$	Water contact angle	°

List of Acronyms

CCM	Catalyst Coated Membrane
CV	Cyclic Voltammetry
DLR	Deutsches Zentrum für Luft- und Raumfahrt
DMFC	Direct Methanol Fuel Cell
EDX	Energy Dispersive X-Ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
FEP	Fluorinated ethylene propylene
GDL	Gas Diffusion Layer
LSV	Linear Sweep Voltammetry
MEA	Membrane Electrode Assembly
MPL	Micro Porous Layer
OCP	Open Circuit Potential
PEM	Proton Exchange Membrane
PEMFC	Proton Exchange Membrane Fuel Cell
PTFE	Polytetrafluoroethylene
RH	Relative Humidity
SEM	Scanning Electron Microscopy

1 Introduction

1.1 Framing and presentation of the work

Proton Exchange Membrane Fuel Cells (**PEMFCs**) are technologies which convert chemical energy into electricity. They are viewed as displaying a great potential for the decarbonization of the energy for mobility. PEMFCs hold high power densities and environmental benefits, allowing them to be applied in various fields, such as the automotive, stationary and portable equipment.

In a PEMFC, an oxidation (at the anode side) and a reduction (at the cathode side) reaction occur so that water is generated at the cathode side. Hydrogen, at the anode, permeates through the porous diffusion media, splitting into protons and electrons. The electrons travel through an external circuit and protons proceed to the membrane, combining with oxygen in the cathode side to produce water.

Despite the technological advances and efforts to make the PEMFC commercially available, this technology still faces some challenges, such as the water management, at the cathode side. Liquid water tends to accumulate at this side of the fuel cell, blocking the pores of the diffusion media and limiting the gas transport. This results in mass transport losses and the performance of the PEMFC is affected. A good balance is required to allow the effective removal of water away from the catalyst layer, maintaining at the same time the hydration of the membrane and allowing better proton conductivity.

The Gas Diffusion Layer (**GDL**) is a porous carbon composite material and plays a crucial role in the water management and, consequently, in the overall performance of the PEMFCs. This component acts as a functional and support structure for the membrane electrode assembly (**MEA**), the core of the PEMFC. The GDL is responsible for the efficient transportation of the reactant gas, from the flow channels to the catalyst layer; draining out liquid water at the same time. Additionally, it provides the conduction of electrons with low resistance and is impregnated with a hydrophobicity agent which facilitates the water removal.

The GDL consists of a macro porous substrate and can be coated with a micro porous layer (**MPL**). It was observed that the addition of a MPL results in an effective water management in the MEA, thereby improving the overall performance of the PEMFC. This layer reduces the liquid water saturation, suppressing therefore severe water flooding at the cathode side. The optimization of its functional properties is only possible if the role of its key parameters is well understood. These include structure, porosity, hydrophobicity and hydrophilicity, gas permeability, transport properties, water management and the surface morphology. Thus,

regarding the role of the MPL in the fuel cells' efficiency, further understanding is required through innovative research, focusing most in its characterization.

Laser modification of the MPL is a promising technique that allows the creation of specific hydrophilic pathways, resulting in the enhancement of the liquid water transport during PEMFC operation and, consequently, an increase in its performance. Different laser output powers and laser process speeds can be applied, according to the desired effect. An optimization of these parameters leads to a new modified GDL, with different structural properties that could enhance the performance of a PEMFC, when assembled in its cathode side.

Studies on the hydrophobicity and wettability of the inner surfaces in the laser structured GDLs are based on the measurement of contact angles. Through the combination of the Washburn and the Owens-Wendt models, the internal contact angle of water can be extrapolated, allowing a better comprehension of the hydrophobic properties and the wettability of this structure.

The quantification of the hydrophobicity and the wettability of the laser modified MPLs is necessary for relating the performance of the PEMFCs with these parameters and for numerical simulation models, giving a great contribute to the progress towards the development of these technologies.

1.2 Deutsches Zentrum für Luft- und Raumfahrt (DLR)

DLR is the German Aerospace Center, with its headquarters located in Cologne. It is an aeronautics and space research center for energy, transportation and aerospace, centering its focus in the fields of aeronautics, space, energy, transportation, digitalization and security. DLR is composed by 40 institutes, with various operational facilities around Germany and international offices in Paris, Brussels, Tokyo and Washington D.C.

The present work was carried out at the DLR's site in Stuttgart, where 6 institutes and about 750 employees are involved, playing an important role in the scientific community of Stuttgart. In addition, it provides a strong educational sector, due to its geographical proximity with the Vaihingen Campus of the University of Stuttgart.

The Institute of Engineering Thermodynamics focuses its main research in the fields of efficient energy storage systems, that conserve natural resources, and next generation energy conversion technologies. The projects that are carried out at the institute act on the development of more efficient electrochemical storage and conversion devices, such as electrolyzers, fuel cells and advanced batteries. The main objectives involve the enhancement of these electrochemical technologies, regarding efficiency, durability, safety,

reliability and cost reduction. In addition to a group of scientific and technical employees, engineers and doctoral candidates, this institute counts with three more research facilities, located in Cologne, Ulm and Hamburg.

1.3 Contributions of the Work

The present work derives from Project IMPALA (IMprove Pemfc with Advanced water management and gas diffusion Layers for Automotive application), developed with the aim of increasing the performance of PEMFCs by improving the GDL, consequently allowing a better understanding of the water management within the MEA. Thus, a new and improved GDL (#IMPALA30) has been developed; resulting in an overall increased performance of the cell (a power density of $1.0 \text{ W}\cdot\text{cm}^{-2}$ was reached). This project was validated at both laboratory and industrial scale and, with the improvement obtained, the stack cost was significantly reduced (up to -7 %). Project IMPALA concluded that laser grafting of the MPL was a promising, scalable and feasible technique that can show even more promising results (particularly at high loads and humidification levels) but that must be adapted to each GDL brand. Also, the exact pattern to apply, laser power and laser process speed were parameters still unclear to the optimization of the GDL. In addition, some complementary work regarding modelling and characterization of the MPL was also required and suggested for future work.

Christina Schmitt developed her master thesis at DLR with the main objective of investigating this laser modification technique and optimizing the parameters mentioned above. Being responsible for the set-up of the laser irradiation installation, Christina observed that amongst the applied laser process speeds of 0.1, 1, and $10 \text{ mm}\cdot\text{s}^{-1}$, the best results were obtained for medium values and a moderate laser power.

My contribution for this work started at this point. Based on some of these optimal parameters, I could improve the laser pattern to be applied in the MPL and observe the overall performance in the fuel cell. I could also start my work varying the laser velocity speed in the smaller range ($1 \text{ to } 10 \text{ mm}\cdot\text{s}^{-1}$), since it had already been concluded that better results were observed between these laser speeds. This helped with the acquisition of even more data to be inserted in future modelling, since the role of the MPL is still not clear, neither its effects on the water management. Mainly focusing on the characterization of the MPL, the internal contact angles were also determined, not only for unmodified GDLs (as IMPALA project tested) but also with the new laser-modified ones. All this data is set to be used in future DLR's simulation models. In addition, I was responsible for building the experimental set-up for a different laser equipment, due to defects observed in the original one.

All the following described work was performed by me. The Energy Dispersive X-Ray Spectroscopy images were obtained by a DLR's technician, with my contribution.

1.4 Organization of the thesis

This thesis is divided into six chapters: Introduction, Context and State of the art, Materials and Methods, Results and discussion, Conclusion and Assessment of the work done.

The first chapter describes briefly the overall problem under study, focusing then in the specific subject of this work, followed by the presentation of the host institution where it was carried out. The Context and State of the Art chapter aims to present the problem in a more global context, addressing all relevant aspects of the work. Literature review of considered methods and technologies is also presented here. The materials and methods used for the development of this work are presented in the third chapter, describing the experimental work carried out. The main results obtained are analyzed and discussed in detail in the fourth chapter and the main results achieved with this work are presented in the Conclusion. The final chapter describes the accomplishments reached with the work performed and provides recommendations for future work.

2 Context and State of the Art

2.1 Fuel Cells

In the last years, an increasing development in both the industrial and technological sectors has been observed: consequently, the world energy demand is growing at high rates. The use of fossil fuels is related to environmental impacts, since they are responsible for the emission of greenhouse gases and other pollutants. It is urgent, therefore, that the industrialized countries seek for new solutions towards the development of new energy systems involving renewable energy sources [1]. The challenge is thus to develop clean, efficient, easily accessible and rechargeable power-generating systems from renewable sources.

A fuel cell is a technology for clean and efficient power generation, since it is responsible for the conversion of the free energy of a chemical reaction directly into electrical energy, allowing high-power densities. The commonly fuels used in fuel cells are hydrogen, methanol and ethanol, among others. Fuel cells find numerous applications, being the fuel cell vehicles one of the most promising ones, since they can function in an environmentally sustainable form. The main advantages of fuel cells, in comparison with other used technologies, include a higher efficiency, no emissions of environmental polluting gases (such as carbon dioxide, carbon monoxide, sulphur and nitrogen oxides, among others) [2]. However, there are still some challenges to overcome, such as hydrogen supply, the fuel cell system cost and its durability [3].

Fuel cells are classified according to different parameters related to operating conditions and structure. The most commonly used are the Proton Exchange Membrane Fuel Cells (**PEMFCs**) and the Direct Methanol Fuel Cells (**DMFCs**), with a similar functioning to the PEMFCs. Other types of fuel cells include the alkaline, phosphoric acid, molten carbonate and solid oxide fuel cells [2], [4]. The functioning of a PEMFC is approached in the following topics in a more detailed way, since it is subject of this work.

2.1.1 Proton Exchange Membrane Fuel Cells

PEMFCs are technologies under intense development towards the enhancement of its performance, efficiency, reliability, manufacturability and cost-effectiveness [5]. Thus, the “iron triangle” for these cells is commonly talked about: it refers to performance, durability and cost [2]. The high cost associated with this technology is mainly due to the expensive perfluorinated Proton Exchange Membrane (**PEM**), which only operates efficiently under fully hydrated conditions. Therefore, big efforts are being made to reduce the cost of the membrane, allowing the commercial availability of these cells.

In a PEMFC, H_2 gas (humidified) is supplied through the flow fields in the bipolar plate. H_2 permeates then through the porous diffusion media into the anode electrode, breaking down into protons and electrons. The electrons travel through an external circuit, driving the load, and the protons permeate through the PEM. Here, they combine with oxygen on the cathode side, producing water [4]. Figure 1 represents, schematically, the main functioning of the PEMFC. These cells have an operating temperature between 50 and 80 °C, an approximate power density of $1 \text{ W}\cdot\text{cm}^{-2}$ ($1.5 \text{ A}\cdot\text{cm}^{-2}$) has already been reached by some projects, a capital cost near $150 \text{ €}\cdot\text{kW}^{-1}$ and are mainly used for portable, mobile and stationary applications [32].

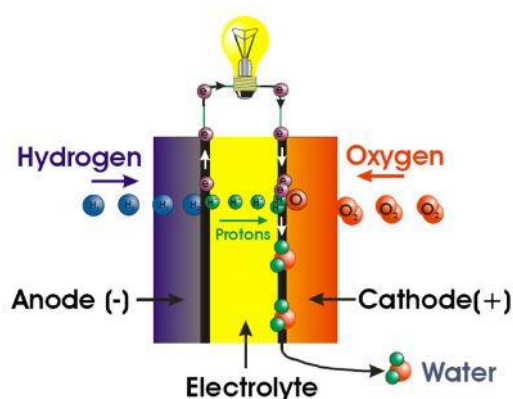


Figure 1 - Schematic design of the PEMFC functioning [2].

PEMFCs design faces a major challenge nowadays which is the water management, responsible for the flooding and the mass transport limitations, especially at the cathode side and at high current densities. Consequently, the overall performance of the cells is affected.

For a good water management, a delicate balance is required: on one hand, the PEM needs to be well hydrated; therefore, water is always necessary to maintain good proton conductivity. On the other hand, the accumulation of excessive liquid water in the pores of the GDL, due to a long operation or even a large output current, limits the gas transport to the catalyst layers, resulting in mass transport losses and a decrease in the power density [5], [6]. A good balance between these two conditions permits the effective removal of water away from the catalyst layer, maintaining at the same time the hydration of the membrane and allowing better proton conductivity. It is of great importance that this balance is not compromised, by managing the amount of moisture at the cathode side, where water is generated [7].

To sum up, it is necessary to understand better how the water distribution works within the GDL. This analysis can be improved by optimizing the water transport properties of the GDL. One way for studying these complex systems is to develop computational models, which could help understanding the water flow in the GDLs. However, and due to the lack of data for the various fibrous materials that form the diffusion media, further efforts are required.

In the PEMFC, two main reactions occur, the oxidation (at the anode side) and the reduction one (at the cathode side), represented by Equations (2.1) and (2.2) for the anode and cathode electrodes, respectively. During the electrochemical reaction, H_2 , in the anode electrode, is oxidized into protons and electrons. The electrons are released, moving through the external circuit towards the cathode. Here, the reduction reaction takes place, combining protons and electrons with O_2 , generating water [2]. The general reaction for the PEMFC is represented by Equation 2.3.



The individual components of the fuel cell must be assembled together to convert energy in a continuous and efficient way. The key components of a PEMFC are the bipolar plates, the sealing media and the Membrane Electrode Assembly (**MEA**).

The bipolar plates provide the paths for the fuel and the oxidant to reach the MEA allowing, simultaneously, the removal of the reaction products. They work as a current collector and are connected to the external circuit. They also provide mechanical stability to the entire assembly [4].

The sealing media is placed between the MEA and the bipolar plates. Its main function consists in preventing any exchange of either fuel or oxidant between the fuel cell and the environment.

Figure 2 sketches a typical MEA, the core of a PEMFC, since it is where the electrochemical reactions occur. The MEA comprehends the PEM, with a layer of catalyst on both sides, and a Gas Diffusion Layer (**GDL**) in contact with each of the catalyst layers. The catalysts on each side allow reactions, while the membrane allows protons to pass through, while keeping the gases separate. This way, the cell potential is maintained, and current is drawn from the cell to produce electricity. There are two types of MEAs, depending on where the catalyst ink is deposited to form the electrode. Thus, there is the Catalyst Coated Membrane (**CCM**), where catalyst ink is coated directly onto the membrane, and the catalyst coated substrate, where the catalyst ink is coated onto the diffusion media to form an electrode.

Sealing material, for instances, ice-cube gaskets are applied to provide correct compression during MEA assembly, acting simultaneously as a barrier for potential leaks.

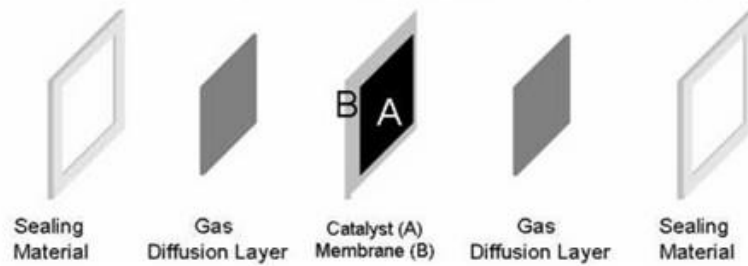


Figure 2 - MEA main configuration (adapted from [8]).

The membrane is responsible for the transport of protons from the anode to the cathode, without passing the electrons that were removed from the H_2 atoms. Additionally, the PEM provides a strong mechanical, chemical and electrochemical stability; offering at the same time a long life, low reactant permeability, high proton conductivity, low electronic conductivity and an effective electrical insulator [2], [4]. The typical used catalyst is platinum (Pt), since it is the most effective one for both oxidation and reduction reactions, and the catalyst loading at each electrode is normally between 0.25 and $0.35 \text{ mg}_{\text{Pt}} \cdot \text{cm}^{-2}$ [32].

The electrodes are part of the MEA and are porous structures of catalyst particles, dispersed in a binder medium. They allow adequate pathways for diffusion of the reactant media to the catalyst site, removal of the reaction products and a good protonic and electrical conductivity [4]. The role of the GDL will be explained in detail in the following topic.

2.2 Gas diffusion Layer

The GDL is a critical component of the MEA and, consequently, of the PEMFC structure, in terms of water management and overall performance of the cells. The understanding of its functionality is of most importance for its optimization. Thus, innovative research and analysis of the GDLs' functional properties (such as structure, porosity, hydrophobicity, hydrophilicity, gas permeability, transport properties, water management and the surface morphology) is essential [9].

This important component has a porous structure that allows the transport of reactant gas from the flow field over to the catalyst sites, acting at the same time as the functional and support structure for the MEA. In addition, the GDL drains out the liquid water from the catalyst layers to the flow channels, conducting electrons and keeping the membrane at wet conditions and low humidity. A GDL is characterized by a good gas diffusion, porosity, air permeability, electrical conductivity, high mechanical integrity and good durability, at various operating conditions. They have therefore a significant role and consequent impact in the performance of the fuel cells, having numerous studies regarding their characterization, status and future directions [9].

A GDL is normally constituted by either carbon fibre cloth or non-woven cloth, since these materials are conductive and resistant to chemical corrosion [4]. Common pore sizes range between 1 and 100 μm and the thickness between 170 and 400 μm [5], [9].

The GDL corresponds to the combination of a macro porous layer and a Micro Porous Layer (MPL), usually coated above it. The role of the MPL is crucial in the water management within the MEA [10]. For purposes of this work, both GDL and MPL terms are used and it is always implied that the GDL has the MPL englobed in its structure. Figure 3 presents the schematic design of the GDL, highlighting the different layers that compose it. When assembled with the MEA, the GDL requires controlled compressibility, to support the external forces from the assembly and to prevent deformation.

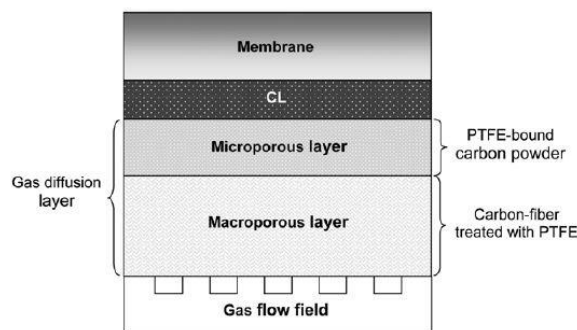


Figure 3 - Schematic design of the multi-layered GDL [11].

The MPL consists in an amorphous mixture of both carbon particles and PTFE [5], [12]. A GDL can have one or more MPLs in its structure, since the addition of this layer enhances the electrical conductivity and the contact with the catalyst layer, improving the water management (especially at the cathode side in the PEMFC) [5], [9].

Both GDL and MPL are usually treated with polytetrafluoroethylene (PTFE), or Teflon, a polymer which gives them its hydrophobic properties. With the addition of PTFE, both gas and water transport are enhanced, since it prevents the excessive water accumulation in the pores of the GDL. However, an excessive PTFE loading can lead to a high level of flooding in the catalyst layer, affecting also the mass transport of the reactant media to the catalyst layers and the overall performance of the PEMFCs. An optimized PTFE content of GDL could result in an effective water management and improved oxygen diffusion kinetics in the MEA. Fluorinated ethylene propylene (FEP) is also a good hydrophobizing agent for hydrophobic treatment. When compared to PTFE, FEP has a superior radiation resistance, better reaction kinetics and higher hydrophobicity [13].

2.2.1 Structural modification of the micro porous layer

The MPL, as mentioned above, is an important component and its role in the performance of fuel cells is a topic in need of further and greater investigation. The efforts that have been made to improve and optimize the MPL's performance involve, for instance, laser modifications.

Numerous studies have been found in the literature, regarding the laser modification of the MPL, which were carefully analyzed and considered for the realization of this work. It has been observed, for all these studies, that laser modification in fact enhances the performance of the PEMFCs and is a technique that should be continued and optimized. However, there are still some disagreements in terms of which technique should be adopted to achieve greater gain in performance. Despite this, all of them appear to agree that the laser modification should be on the cathode-side GDL, where the water management issue is critical. Laser treatment with the aim of obtaining localized water redistribution, by the introduction of hydrophilic regions, can be applied with or without perforations (instead, continuous lines are applied).

Evidences were found that perforations could lead to an increase in degradation in the catalyst layer [13]. However, many authors defend that this technique is, in fact, a promising approach and thus should be reinforced to better understand and optimize the performance of the fuel cell, since it can lead to a decrease in the mass transportation losses [10], [14], [15]. Non-perforating laser modification, on the other hand, is considered a less invasive approach, avoiding then a perforation and obtaining instead a hydrophilic zone: degradation is avoided, and it is still possible to achieve good performance. Thus, this technique is proved to have its advantages on the overall performance of the fuel cells. The laser beams are highly directional, have high power density and better focusing characteristics, unlike ordinary light [16]. The heat of the beam laser is responsible for the weakening (or melting) of the structure and the fibers of the material are consequently detached, however, its effects on a specific structure depend on the exposure time and the physical and geometrical properties of the sample. Lasers are classified according to different classes, according to their maximum output power. Laser products classes 3B and 4 are the most hazardous, with output powers from 5 to >500 mW and are the ones used in this work [17], [18].

Other structural modifications regarding the structure of the MPL involve different techniques, such as the addition of carbon nanotubes to the MPL: it was observed an enhancement in the electrical conductivity and both gas and liquid water transport properties, resulting consequently that higher current densities can be achieved, for different humidity conditions [19]. To modify the properties of the GDL, changes in the hydrophobic treatment, MPL ink formulation and gradients of porosity/wettability, among others, were

also analysed and studied. Innovative modelling (specifically, the pore network modelling) to visualize, in 3D, the liquid pattern within the GDL for ex-situ (capillary injection) and operando (operating cell) situations is one of the most studied so far.

All the techniques presented in this topic are target of future developments and most of them are scalable for mass production, allowing the development of both homogeneous and non-homogeneous GDLs.

2.3 Fuel cells characterization techniques

A wide range of experimental techniques are applied to understand better the fundamentals of a PEMFC. Thus, both electrochemical and physical methods provide an additional analysis of the operating parameters that influence the functioning and the performance of these cells [20].

2.3.1 *In-situ* techniques

In-situ, or electrochemical, characterization methods are carried out to investigate the performance achieved during operation, using a specific material. These tests include the polarization curve, the Electrochemical Impedance Spectroscopy (EIS), Cyclic Voltammetry (CV) and the measurement of the current density distribution, among others. The last three methods referenced above were not carried out in this work, and thus a brief explanation will be given for each one of them.

A polarization curve provides knowledge about the performance losses in the cell, under operating conditions, and other fundamental characteristics [20]. A steady-state polarization curve is obtained by recording the cell potential; it is then plotted as the current density varies and the data is normally recorded under operating conditions like those of real applications. In an ideal polarization curve, 3 major regions can be well-identified, as observed in Figure 4: the activation polarization region, the ohmic polarization region and the concentration polarization region, represented by the numbers 1, 2 and 3 in the figure, respectively.

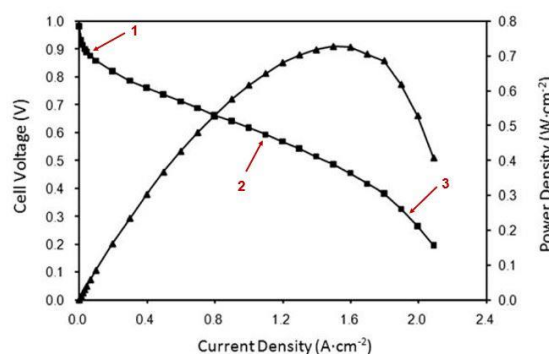


Figure 4 - Typical polarization curve for a PEMFC (adapted from [21]).

The activation polarization region occurs for low current densities. The potential losses here are explained by the kinetics involved in the electrochemical reactions for the fuel cells. The ohmic polarization region characterizes the behaviour at intermediate values of the current density. This region is linear, characteristic of potential loss induced by ohmic resistance to the flow of electrons through the electrodes [20]. Finally, the concentration (or mass transport) polarization region, at high current densities, is where mass transport limitations normally occur. The voltage loss in this region is explained by the spatial variations in the reactant concentration, if they are consumed faster than they can diffuse into the porous electrode. Voltage losses here can also be due to variations in the bulk flow composition.

This curve can be converted into a power density plot, also represented in Figure 4. This is obtained by simply multiplying the cell potential by the current density, in each point obtained. Both nominal and maximum power of the cell can be determined by the analysis of the power density curve.

Regarding the other *in-situ* methods mentioned above, in the EIS a polarization resistance is assigned to the system, based in an electrical current which passes through the electrochemical cell. When this happens, the cell voltage deviates from its equilibrium value (U_{ocv}) under open-circuit conditions.

CV is a measurement technique which characterizes the cell and determines the prevailing degradation process, since this phenomenon results in performance loss of the fuel cell [1], [20]. CV provides information about the electrochemical active area, the double-layer characteristics and the hydrogen fuel crossover through the membrane. The measurement of the current density distribution is another method which allows the detection of critical conditions within the fuel cells, since undesired side reactions occur under starving conditions, caused by a non-homogeneous distribution of the reactant gases, temperature and local water content across the active area [1], [20].

Linear Sweep Voltammetry (LSV) is another *in-situ* method that allows the study of the behavior of the fuel cell, allowing, for example, the detection of H_2 crossover or any internal short circuit between the anode and the cathode [20], [22].

2.3.2 *Ex-situ* techniques

Ex-situ, or physical, characterization methods allow the detailed characterization of both structure and properties of the individual components that compose the PEMFC. These include the Energy Dispersive X-Ray Spectroscopy (EDX), the Scanning Electron Microscopy (SEM) and the mercury porosimetrie, among other techniques. These last two methods were not carried out in this work.

The SEM technique allows the determination of the surfaces' morphology and effects on the structure, as well as other properties of the sample. It is an *ex-situ* method that can be applied to various components of the cell. The samples must be cut, embedded, ground and polished to a good analysis of its microstructure, layer thickness, material interactions and the formation of, for example, foreign phases. These parameters can all be characterized either by SEM or EDX [1]. By using, additionally, the EDX analysis, the chemical compositions can also be analyzed.

EDX measurements allow the identification of the chemical composition of a specific sample (in the case of this work, the PTFE distribution in the GDLs). In this technique, the X-Ray beams interact with each element and a response is detected and recorded as a graph. Afterwards, and with the characteristic energy of each element's signal and corresponding intensity, the relative compositions of the sample can be determined [1].

The mercury porosimetry method evaluates the pore size distribution and pore geometry. Thus, the bulk porosity of the GDL (the total pore volume divided by the summation of its total pore volume and its solid volume) can be determined, by measuring the amount of mercury that penetrates the pores of a porous media, as a function of the applied pressure.

Other common used methods include the immersion technique [9], in which the sample is weighted before and after immersing in a wetting liquid; and neutron radiography, one the most complex methods used for the physical characterization and that provides sustainable information about the inner properties, such as the pore size distribution and internal wettability [6].

2.4 Wettability of the inner surfaces

GDLs should display mixed wettability, since their composition is heterogeneous: hydrophilic carbon fibres and hydrophobic PTFE agglomerates, having a great impact in the water transport [7].

Ideally, the GDLs should be structured in such a way that the transport of liquid water inside them is carried out through specific hydrophilic pathways, with the lowest capillary pressure possible, while the gas reactants follow hydrophobic routes, free of condensed water. This is usually obtained applying specific methods for the creation of arranged hydrophilic/hydrophobic pathways [6], [23]. Figure 5 shows the pathways of a conventional GDL, which are often tortuous (in the left), in contrast with a modified GDL (in the right side), where the pathways for both liquid water, in blue, and for reactant gases, in green, are well defined and aligned [6].

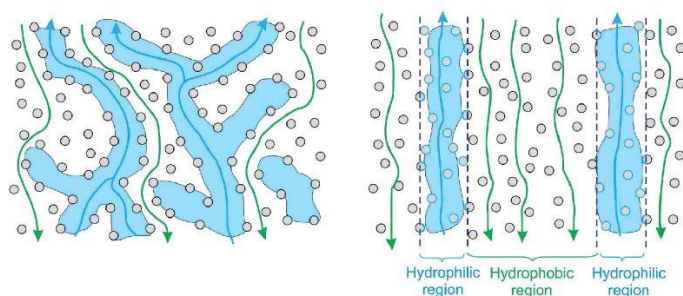


Figure 5 - Schematic design of a GDL with tortuous (left) and defined (right) pathways [6].

The characterization of the wetting properties of the GDLs are therefore of crucial importance for the operation and overall performance of the PEMFCs. The wettability of the inner surfaces is related to the internal contact angle, θ , of water and the surface tension. Thus, a classic way to characterize wettability is based on the water contact angle, $\theta_{\text{H}_2\text{O}}$. However, it is not possible to obtain it experimentally, since GDLs are too hydrophobic; thus, $\theta_{\text{H}_2\text{O}}$ is computed from the contact angle of different solvents and then extrapolated to water, using an appropriate model such as the Washburn or the Owens-Wendt.

2.4.1 Washburn method

The Washburn method is a technique based on the measurement of the increase in mass of a porous solid, caused by the advancement of a liquid inside its pores (due to the capillary forces). It models the experimental data by means of the modified Lucas-Washburn equation (Equation 2.4), which describes the capillary rise of a liquid in a porous material when inertia and gravitational forces are negligible [24].

$$\cos \theta = \frac{m^2}{t} \frac{\mu}{C_W \rho^2 \sigma_{LV}} \quad (2.4)$$

In this equation, θ is the internal contact angle between a liquid and the pores of the material (in this work, the GDL), m is the mass of liquid absorbed by the sample during the time t , μ is the dynamic viscosity, ρ is the density and σ_{LV} is the liquid/vapour surface tension. C_W is the Washburn (or capillary) constant, determined from a reference solvent.

In a typical Washburn experiment, the samples must be initially tested with a low surface tension and short straight-chain alkane, with assumed complete wettability. This means that they have a null value for the contact angle and, thus, $\cos \theta = 1$ [5]. Such liquid is set as the reference solvent. n-pentane, n-octane, n-hexane or n-heptane are examples of such solvents with complete wettability. Based on the reference solvent properties and using the modified Washburn equation, the value of C_W can be determined. This value is then assumed to be the same for all the other liquid tests involved in the experiments. Afterwards, and combining the data obtained (m^2 vs. t) with Equation 2.4, the values for θ between various liquids and the GDL pores can be calculated.

From the determined values of θ , one of two situations can occur: if the value is less than 90° , then the wettability is favoured (leading to a more hydrophilic behaviour) and will be strongly favoured as lower as θ is and as higher as σ_{LV} is. The inverse situation occurs for θ superior to 90° .

For the extrapolation of θ_{H_2O} , the Zisman's theory is normally applied. This takes in account the cosine of the contact angle of different liquids, estimated through the Washburn method, and their surface tension. Figure 6 evidences a typical Zisman plot, highlighting the reference solvent as the one to have perfect wettability and a possible set of wetting fluids that can be used. Their surface tension values should be equally distributed along the plot, until a fair approximation to water is made and its contact angle, θ_{H_2O} , can be extrapolated.

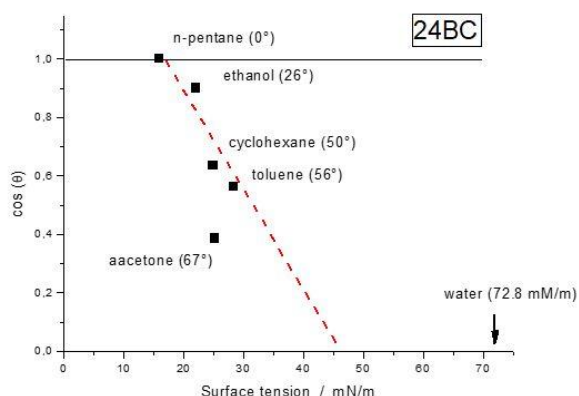


Figure 6 - Typical Zisman plot (from IMPALA project).

The Washburn method has some limitations, especially when applied to thin porous films like the GDLs [24]: for instances, water cannot be used as a test liquid, since GDLs are typically hydrophobic and, when performing the measurements, m^2 vs. t is no longer linear, as predicted by the Lucas-Washburn Equation.

The evaporation losses through the surface of the sample, during the experiments, also present a barrier towards the final goal. Thus, the evaluation of the contact angles is not enough based only in the Washburn method and other models should be combined to a better water extrapolation.

2.4.2 Owens-Wendt two-parameter model of surface tension

The evaluation of the average internal contact angle of water, θ_{H_2O} , within the pores of the GDL can be determined combining both the Washburn method and the Owens-Wendt two-parameter model of surface tension, allowing a better evaluation and prediction of the wettability [24].

The Owens-Wendt theory accounts for site specific interactions between solid surfaces and liquids. Thus, the surface tensions of the liquid/vapour and solid/vapour interfaces (σ_{LV} and σ_{SV} , respectively) are distributed by two components: a dispersive and a polar one, as suggested by Equations (2.5) and (2.6). The first one accounts for Van der Waals and other non-site specific interactions, whereas the second one accounts for dipole-dipole, hydrogen bonding and other site specific interactions [5]. The addition of these two components provides the total surface tension. In the equations presented below, σ_{LV}^{total} is the overall surface tension of the liquid, with σ_{LV}^d and σ_{LV}^p as the dispersive and polar components of this surface tension. The same applies for the overall surface tension of the solid, σ_{SV}^{total} .

$$\sigma_{LV}^{total} = \sigma_{LV}^d + \sigma_{LV}^p \quad (2.5)$$

$$\sigma_{SV}^{total} = \sigma_{SV}^d + \sigma_{SV}^p \quad (2.6)$$

The Owens-Wendt model is a combination of two governing equations: Young's and Good's represented by Equations (2.7) and (2.8), respectively. The Young's equation is originated from balancing the interfacial surface tensions at the three-phase solid/liquid/vapour contact line and Good's equation approximates the solid/liquid component of the surface tension.

$$\sigma_{LV} \cos \theta = \sigma_{SV} + \sigma_{SL} \quad (2.7)$$

$$\sigma_{SL} = \sigma_{SV} + \sigma_{LV} + 2 \left(\sqrt{\sigma_{SV}^d \sigma_{LV}^d} + \sqrt{\sigma_{SV}^p \sigma_{LV}^p} \right) \quad (2.8)$$

Taking in account Equations 2.7 and 2.8, the Owens-Wendt equation is presented (Equation 2.9).

$$(1 + \cos \theta) \left(\frac{\sigma_{LV}^p + \sigma_{LV}^d}{2\sqrt{\sigma_{LV}^d}} \right) = \sqrt{\sigma_{SV}^d} + \sqrt{\sigma_{SV}^p} \times \sqrt{\frac{\sigma_{LV}^p}{\sigma_{LV}^d}} \quad (2.9)$$

The plot of Equation 2.9 provides a better extrapolation of θ_{H_2O} , in contrast with the use of the Washburn method only. Therefore, a linear regression fit (for several different liquids) yields the solid/vapour surface tension components: $\sqrt{\sigma_{SV}^p}$ is provided by the slope and $\sqrt{\sigma_{SV}^d}$ from the intercept. Once these values are found, the final average internal contact angle of water on the GDL is determined.

The combination of the Washburn method and the Owens-Wendt two-parameters theory has been demonstrated to be a successful way to estimate both the internal contact angle to water and the surface energy of GDL materials [5].

3 Materials and Methods

3.1 Laser modification of the Gas Diffusion Layer (GDL)

Figure 7 shows the experimental set-up used for the laser modification experiments conducted. For this work, two different lasers were used: a class 3B (represented in the figure) and a class 4 one, where the experimental set-up is the same for both. The lasers are green diode pumped solid state ones, providing high output power and low noise. These are devices with high-voltage and its improper use can lead to the exposure of potentially lethal voltages. Precautions must be assured to avoid electrical injuries or damages to the equipment.

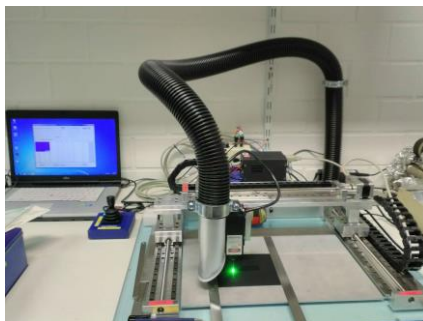


Figure 7 - Experimental installation for the laser modification of the MPLs.

The laser, as suggested by the image, is directed at the surface of the MPL and moved around to apply the desired pattern. To the left of the laser there is a filter which prevents the emerging gases and particles, from the removal of the PTFE, to escape, allowing its extraction. This filter technology, supplied by ULT[®], has an extraction arm for an efficient detection of welding fumes, as suggested by the image. Both the laser and the filter are placed in a XY bridge (supplied by MOVTEC[®]) that can move around by the commands of a joystick. Therefore, the sample is positioned in the desired location and the laser goes towards it. The laser requires a power supply and the set for the intended laser power is defined there, by means of a potentiometer. As two different classes of lasers were used (different ranges of laser power), this set had to be changed and the maximum laser power was considered with attention, due to the risks involved when handling with this equipment. The laser sources needed to be switched on at least 10 minutes before the experiments to achieve a constant value of the laser power. Coupled with this set-up there is a computer running software - RasterPos (MOVTEC[®]) - which main features include control and positioning of the laser. It allows the definition of the desired pattern to be applied to the MPL's surface. In addition, the laser process speeds at which the device should run are also defined in this program. Therefore, the modification can be carried out automatically.

3.1.1 Laser modification using a class 3B laser

The first laser modifications were performed using a class 3B laser product, which is hazardous for eye exposure and it can heat both skin and materials (class 3B lasers are not considered a burn hazard). The beam location should be kept away from people's eyes and heads. Therefore, the laser was used with extreme care and with laser protective glasses. Class 3B lasers have an output power that goes between 5 and 499 mW [17]. The class 3B laser used in this work was provided by DHOM® (Suzhou Daheng Optics & Fine Mechanics Co., Ltd) and it has a wavelength of 532 nm and an output power of 300 mW (DHOM-W532-300mW). The GDL samples were supplied by SGL Group - The Carbon Company®, coated with a MPL layer on one side. Its main characteristics can be found in Table 1.

Table 1 - Specifications of the GDL samples used in the laser modification.

GDL	Characteristics	Thickness (μm)
25 BC "DECODE" ¹	MPL marking on substrate; Non-woven fabric	235

The experiments with this laser were carried out with an output power set of 600 mW (at the potentiometer), the correspondent to a laser power of ca. 250 mW. The laser modification consisted in applying a defined pattern, shown in Figure 8, in the MPL's surface, at a specific laser velocity speed.

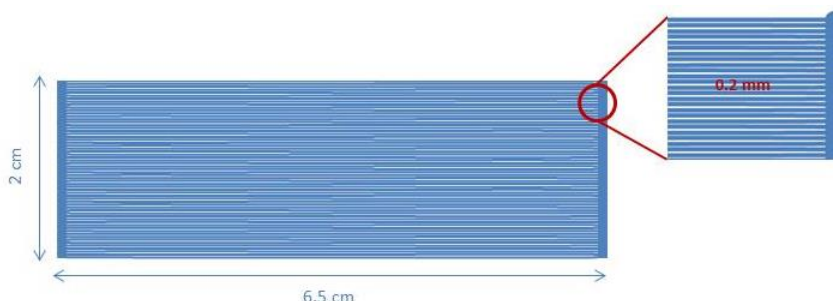


Figure 8 - Standard laser pattern used on 25BC MPL side, in RasterPos (MOVTEC®).

This was the main pattern used for all the experiments and that was englobed in the computers' program associated with the laser. It was chosen with the objective of removing the maximum amount of PTFE content possible: therefore, a total of 200 points (maximum number allowed by the program RasterPos) were selected. As suggested by the image, the pattern was applied to a (6.5×2) cm² dimension samples and it is mainly characterized by continuous lines, spaced 0.2 mm between each other (observed in the zoom in Figure 8). This pattern was applied for different laser velocity speeds: 1, 3, 5 and 10 mm·s⁻¹.

¹ The DECODE (Understanding of Degradation Mechanisms to Improve Components and Design of PEFC) project was carried out at DLR, from 2008 to 2011.

3.1.2 Laser modification using a class 4 laser

The second set of experiments was carried out using a class 4 laser product, which is more powerful than the one used in the previous experiments and has an output power > 500 mW. Skin and eyes are damaged if exposed to the direct or scattered laser beam. Precautions must be taken to avoid injuries from the laser beam to anyone in the work area [18]. The laser was supplied by Changchun New Industries Optoelectronics Technology Co. Ltd[®] and it has a wavelength of 532 nm and an output power of 500 mW (RLTMGL-532-500-3). The beam diameter is 1.333 mm.

Table 2 sums up the two set of experiments carried out for the laser modification of the MPLs, including the type of laser used, the laser velocities applied and the laser power set.

Table 2 - Resume of the laser modification experiments performed.

Experiments	Laser Class	Laser Output Power	Laser velocity (mm · s ⁻¹)
1 st set	3B	ca. 250 mW	1; 3; 5; 10
2 nd set	4	ca. 407 mW	1; 3; 5; 10

3.1.3 Physical characterization of the samples

Energy Dispersive X-Ray Spectroscopy (EDX) images were taken to observe the effects on the structure of the samples, due to the laser modification. For a better comparison of results, a conventional GDL was also analysed.

3.2 Washburn experiments

Figure 9 presents the experimental installation where these experiments took place. Several beakers were filled with approximately 40 mL of different solvents and sealed with paraffin to prevent the liquids' evaporation. As suggested by the image, the beakers were placed on a platform which lifted until the desired position. The modified GDL samples, as well as conventional ones, were held by a metal clamp, which was suspended from a sensitive balance (supplied by Sartorius[®]), connected to a computer. At the time the balance detected contact of the sample with the liquids' surface, the computer program started to record the mass of liquid absorbed as a function of time, for about 5 minutes.

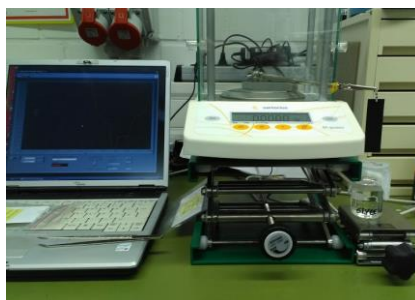


Figure 9 - Experimental installation for the Washburn experiments.

The Washburn experiments consisted in varying either the reference solvent, or the liquid tests. Table 3 resumes all the sets of experiments that were carried out, with the respective liquids used. In Appendix 1 it can be found a brief resume of the most important properties and safety precautions that had to be considered whenever dealing with them. The solvents were supplied either by Merck Millipore or Sigma Aldrich, with purity greater than 99%.

Table 3 - Resume of the Washburn experiments performed.

Experiments	Reference solvent	Liquid tested solvents
1 st ; 2 nd ; 3 rd sets	n-octane; n-hexane; n-heptane	DMSO; THF; 1,4-Dioxane; o-xylene; toluene; glycerol; ethylene glycol
4 th set	n-decane	cyclohexane; n-tetradecane; toluene; nitromethane; methyl benzoate; benzyl alcohol; ethylene glycol; diiodomethane; formamide; glycerol

3.2.1 Owens-Wendt theory

For the third and fourth set of experiments presented in Table 3, the contact angle was extrapolated using the combination of the Washburn with the Owens-Wendt two-parameter surface tension model (Equation 2.9). This last part of the work involved calculations through computational tools (Origin®) and the results are displayed and discussed in the next chapter.

3.3 Electrochemical characterization of the PEM Fuel Cell

Tests in 25 cm² single cells were performed with the objective of evaluating the performance of the PEM fuel cell when assembled with laser modified GDLs on the cathode-side. Polarization curves were taken for different Relative Humidity (RH) conditions, 100, 75 and 50 % RH. The assembly of the MEA consisted in placing an ice-cube gasket at the anode-side of the cell to seal the individual cell components, followed by a standard GDL with a surface area of 25 cm². The membrane was placed on top of the GDL, followed by a second gasket and, finally, the cathode-side GDL. Table 4 presents the main specifications of the components used in this experimental part, except for the GDLs, which was already presented in Table 1. The Catalyst Coated Membrane (CCM) had a catalyst loading of 0.3 mg_{Pt}·cm⁻² (anode and cathode side).

Table 4 - Main specifications of the PEMFC components used.

Component	Specifications	Supplier
Ice-cube gasket 35 FC-PO100	0.5 µm thickness	Quintech®
Nafion membrane XL	27.94 µm thickness; 0.3 mg _{Pt} ·cm ⁻²	Ion Power®
Bipolar plates	Anode side: stainless steel; Cathode side: golden coated stainless steel	DLR

The MEA assembly was performed, manually, in a normal bipolar plate, of stainless steel and gold coated at the cathode-side. In the end plates there are gas inlets and outlets and holes for the thermocouples, to keep the cell's temperature in control. Voltage measurement cables are also englobed in this structure. Both plates have a flow field with a specific channel width and depth. At the end, the cell was closed, and a determined torque ($3.6 \text{ N}\cdot\text{m}^{-1}$ in this work) was applied, in a diagonal way. Figure 10 presents the assembly of the MEA for one of the tests (on the left) and the test bench where the measurements took place (on the right side). When assembling the cathode GDL, the channels created, via laser irradiation, were placed in a perpendicular way towards the flow field of the bipolar plates. All the conditions were maintained constant. The operating anode and cathode flows, as well as the current applied, for the conditioning test, are presented in Table 21 (see Appendix 1).



Figure 10 - Assembly of the MEA in the bipolar plate (left) and the test bench (right).

In the test bench facilities, parameters like pressure, temperature, volume flows and humidity of the reaction gases can be controlled. The H_2 and O_2 bubblers are electrically heated at both sides of the cell and provide the moistening of the gases. They were filled with distilled water, so the gases flow through the heated water and leave the bubbler saturated at the set temperature, depending on which RH conditions are being tested. The outlet pressure at both anode and cathode was set to 1.5 mbar. Table 5 sums up the trials carried out in this work, emphasizing the different RH conditions at which the polarization curves were taken.

Table 5 - Resume of the experiments carried out for the electrochemical characterization.

Experiments	Anode-side GDL	Cathode-side GDL	RH (%)
1 st set	Unmodified GDL	Unmodified GDL	100; 75; 50
2 nd set	Unmodified GDL	Laser modified $v = 1 \text{ mm}\cdot\text{s}^{-1}$	100; 75; 50
3 rd set	Unmodified GDL	Laser modified $v = 3 \text{ mm}\cdot\text{s}^{-1}$	100; 75; 50

4 Results and Discussion

The laser modified GDLs (at laser process speeds of 1, 3, 5 and 10 mm·s⁻¹), as well as conventional GDLs, were analyzed through physical and electrochemical methods. In addition, Washburn experiments were carried out to study its wettability and predict important parameters for future developments. The following topics discuss, in detail, the results obtained.

4.1 Physical characterization of the laser modified GDLs

With the laser modification of the GDLs applied in this work, the optimization of a pattern that would allow the creation of hydrophilic pathways along the surface was a desired objective. This way, liquid water, during PEMFC operation, could be preferably conducted through them and reactant gases would pass independently through the remaining regions. This could be a solution for the water management problem at the cathode side of the PEMFC. Consequently, the overall performance of a PEMFC, when assembled with a laser modified structure, could increase.

The heat of the laser beam allowed the removal of the PTFE content in the surface of the MPL in a more or less intensive way, depending on the laser power and laser process speed applied. A greater heat impact could be observed when a stronger laser output power and a lower speed were applied, and the contrary was observed for low power and higher speeds. As mentioned before, two different classes of lasers were applied: the laser speeds were maintained constant (1, 3, 5 and 10 mm·s⁻¹), whereas the set output power varied: ca. 250 mW for the class 3B laser and ca. 407 mW for the class 4. The velocities were varied in a small range and it was expected that for the lowest velocity, the heat impact would be greater; but not big enough to the point of eliminate the main functions of the GDL. The laser output power was not set to its maximum (again, to prevent the hindering of the main functioning) but instead to an intermediate value.

The laser pattern (see Figure 8) was defined with the aim of obtaining the maximum removal of PTFE content possible, increasing the hydrophilic properties of the structures. Therefore, a maximum of 200 points was set in the program RasterPos and continuous lines were applied throughout the sample, spaced between each other by 0.2 mm. This pattern could not be applied to a 5×5 cm² GDL sample (limited by the program): instead, a 6.5×2 cm² was used. This constituted a barrier for the electrochemical characterization, since this experimental part was held in a 5×5 cm² bipolar plate. Nevertheless, this surface area was useful for the Washburn experiments (where a 5×5 cm² surface area would not be handy).

In Figure 11 it can be observed a sample after laser modification, where the difference between the modified and unmodified areas in the MPL is visible, except within the pattern itself: since the spacing between the lines was so small, the different regions cannot be observed by eye. This lead to need of EDX images, a common used technique that allows not only the analysis of the structure in a more precise way, as well as the distribution of the different elements that compose it. Especially in this case, the distribution of PTFE is of most importance, to verify that, indeed, the laser promoted the removal of fluorine and increased the hydrophilic character of the GDL.

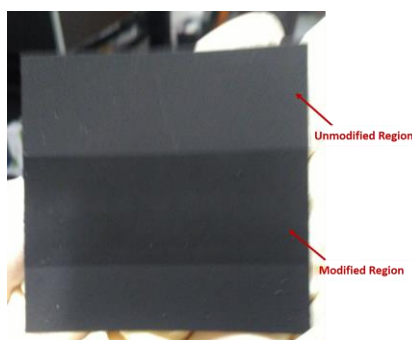


Figure 11 - Laser modified MPL ($v=1\text{mm}\cdot\text{s}^{-1}$), highlighting the different areas of modification.

The difference between the samples that were modified by different laser process speeds is not also visible by eye, reinforcing the need of the EDX measurements. Figure 12 shows the EDX images taken for the laser modified samples. For terms of comparison, a GDL that did not suffer from any laser treatment is also displayed.

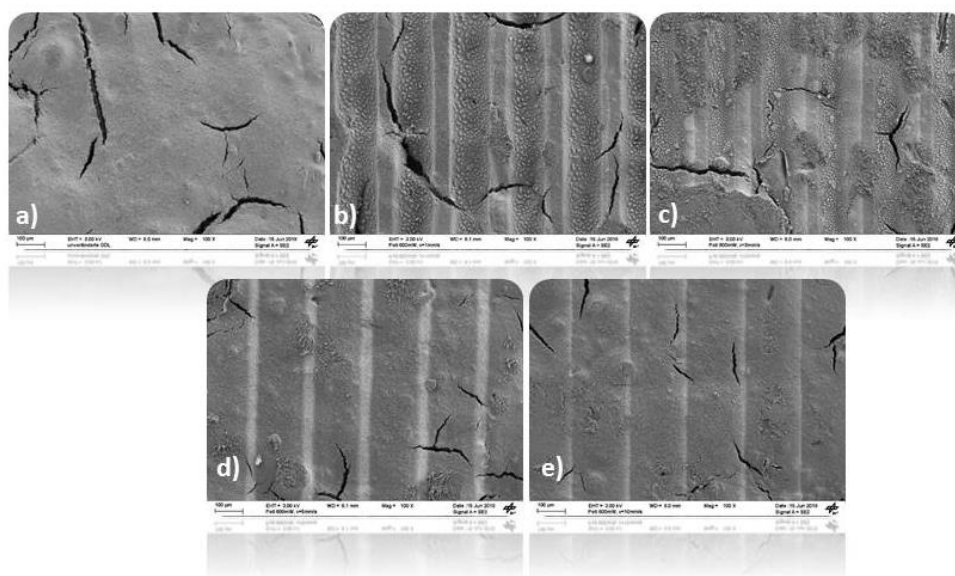


Figure 12 - EDX images of unmodified MPL (a) and laser modified MPLs $v=1\text{ mm}\cdot\text{s}^{-1}$ (b); $v=3\text{ mm}\cdot\text{s}^{-1}$ (c); $v=5\text{ mm}\cdot\text{s}^{-1}$ (d) and $v=10\text{ mm}\cdot\text{s}^{-1}$ (e).

All the samples suffered from the same laser treatment providing therefore the same conditions to a good analysis. Thereby, the laser used was the class 4 one, with the highest

output power. In the EDX images presented in Figure 12 it is possible to see the difference between the heat impacts for each velocity enforced, demonstrating, as expected, that the lowest one ($1 \text{ mm}\cdot\text{s}^{-1}$) is where this heat is more intensive (Figure 12b), when compared to the unmodified one (Figure 12a) and to the remaining samples, at lower velocities. The contrary is observed for the lowest velocity, $10 \text{ mm}\cdot\text{s}^{-1}$ (Figure 12e). For all the samples, it is possible to observe the presence of micro cracks, characteristic of the surface of the MPLs and that function as paths for the efficient transport of liquid water through the GDL [25].

Another feature that the EDX allowed was to observe the presence, or absence, of PTFE in the samples, when submitted to the laser treatment. It was expected to see a decrease in the mass fraction of fluorine, exhibiting that the laser treatment functioned in the correct way. This implies that, by removing the PTFE content, the hydrophilic properties were improved in the specific regions where the laser passed through. Figure 13 shows a conventional GDL, with four regions marked in red: these are the areas where the mass fractions of carbon, oxygen and fluorine were estimated.

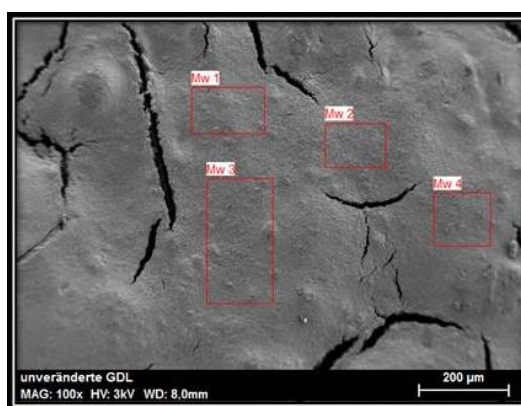


Figure 13 - Unmodified MPL (EDX image) for mass fraction analysis.

Table 6 evidences the EDX measurements corresponding to the sample in Figure 13. This measurement serves as base to compare with the remaining modified samples.

Table 6 - EDX measurements: mass fraction for unmodified MPL.

Region	C	O	F
Mw 1	79.29	0.91	19.80
Mw 2	80.19	0.81	19.00
Mw 3	79.88	0.71	19.40
Mw 4	79.78	1.01	19.21

Figure 14 reveals the analysis considered for the EDX measurements and corresponds to the laser modified structure at laser speed of $1 \text{ mm}\cdot\text{s}^{-1}$. The regions marked in green correspond to unmodified areas (with no laser treatment applied) - Mw 1, 2, 3 and 4 in the images - and

in red the laser-modified ones (Mw 5 to 8). The same applies for the remaining samples (see Figures 27 to 29, in Appendix 2).

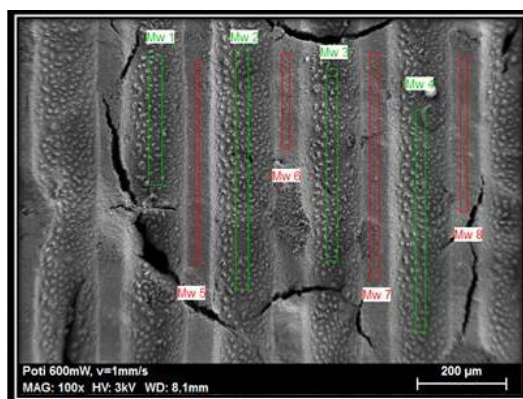


Figure 14 - Laser modified MPL ($v=1 \text{ mm}\cdot\text{s}^{-1}$) for mass fraction analysis.

Table 7 reveals the mass fraction corresponding to Figure 14. It is possible to conclude that the laser treatment functioned as expected, since the percentage of fluorine content dropped when passing from an unmodified to a laser modified area. This denotes that the hydrophilic pathways were successfully created, and that liquid water will be preferably conducted through these (during PEMFC operation), whereas the reactant gases through the unmodified, and hydrophobic, regions. It also shows that the laser treatment completely changed the composition of the structure, which can be related with the heat impact of the laser beam. Thereby, it is very likely that the temperature effects, particularly high temperatures, have an influence in the PTFE content or structure [26]. The presence of a small percentage of sodium, in region Mw 8, can be explained by either the normal presence of this element, due to its abundance on earth, or by the EDX measurement itself, that could have been affected in terms of precision.

Table 7 - EDX measurements: mass fraction for laser modified MPL $v=1 \text{ mm}\cdot\text{s}^{-1}$.

Region	C	O	F	Region	C	O	F	Na
Mw 1	90.56	2.92	6.52	Mw 5	96.52	1.16	2.31	-
Mw 2	92.51	2.30	5.19	Mw 6	95.34	1.23	3.43	-
Mw 3	90.25	3.05	6.70	Mw 7	97.20	1.05	1.76	-
Mw 4	92.49	2.52	4.99	Mw 8	93.43	1.67	3.93	0.97

Regarding the analysis of the EDX measurements for the other samples (see Tables 22 to 24 in Appendix 2), the same conclusions could not be withdrawn: the results were not the expected ones, since the content in fluorine increased in the laser modified areas; instead of decreasing as observed for the laser modified sample velocity $1 \text{ mm}\cdot\text{s}^{-1}$. This was assigned either to experimental errors or to the evaporation of the fluorinated compounds, followed by condensation with concentration at the bottom of the grooves by the laser.

Therefore, it cannot be concluded, for the samples, if the laser indeed act on the surface of the MPL; neither it is possible to relate the effect of the laser modification with the performance of a PEMFC. In addition, the laser treatment showed some disadvantages, especially concerning the pattern applied, due to limited design flexibility. Nevertheless, the physical characterization, by *ex-situ* methods like the EDX, is not the only manner to fully distinguish if the laser treatment was carried out in the correct way or not; thereby, electrochemical characterization is also required and will be discussed in the next topic.

4.2 Electrochemical characterization of the laser modified GDLs

The different laser modified GDLs were placed in the cathode-side of the fuel cell, during the assembly of the MEA, to observe the differences in the overall performance. In the anode side of the cell, a standard GDL was always set, since water management is identified to be more critical on the cathode. The performance of the PEMFCs was analysed for different relative humidity conditions, allowing a good indicative of the influence of the laser modification technique. Thereby, the polarization curves were obtained for 50, 75 and 100 % RH at the anode and the cathode (from low to high humidified reactants, respectively), at controlled cell temperatures. The samples submitted to this experimental part were the laser modified ones, velocities 1 and 3 mm·s⁻¹, and an unmodified GDL (for better comparison of the results).

During the assembly of the MEA, the cathode-side GDL was placed in a specific manner, as observed in Figure 15: the channels, created by the laser treatment, in the surface of the MPL were put in the perpendicular direction to the flow fields of the bipolar plate used for these measurements. As mentioned before, it was not possible to apply the laser modification to a whole 5×5 cm² sample: thus, the pattern applied covered instead a 5×2 cm² surface area. Despite this, it is expected that the performance of the fuel cell increases with this new modification due to the enhancement of water management.

A 25 cm² bipolar plate was used for these experiments. For future work, the use of a segmented bipolar could be useful to better characterize the PEMFC, since it allows the visualization of the current density distribution.

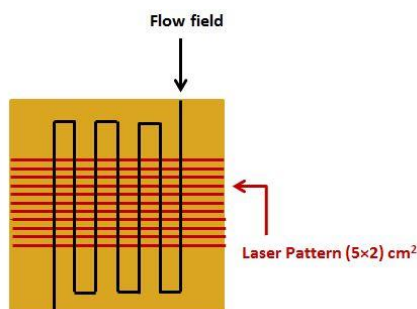


Figure 15 - Schematic representation of the laser modified GDL for the cathode side of the PEMFC.

The polarization curves for 100 % RH corresponds to a temperature of the cell and humidifiers (anode and cathode side) of 80 °C - the anode and cathode gases were both fully humidified before entering the cell - and it is obtained experimentally, by giving input of the current and withdraw the corresponding potential, after the stabilization for that point. Afterwards, the curve is presented related to the area of the fuel cell where the operation was carried out (in this case, to a 25 cm² PEMFC).

Figure 16 evidences the polarization and power density curves for 100 % RH conditions, for the same fuel cell, assembled with either an unmodified or laser modified GDLs, with different laser velocity speeds applied. From the analysis of the polarization curves it is clearly visible that the trial that resulted in better performance is for the PEMFC assembled with the laser modified GDL at velocity 1 mm·s⁻¹. This increase in the performance, when compared to a PEMFC containing a non-modified GDL, meets the expectations: it can be assumed that the laser modification had a beneficial effect towards water management and enhanced the overall performance. It is a good indicative that this laser technique should be further studied, since promising results can be achieved.

Regarding the sample that suffered laser treatment at a process speed of 3 mm·s⁻¹, the same could not be concluded: at 100 % RH, the performance demonstrated to be lower than the unmodified one. This can be explained by some flooding issues that may have occurred during fuel cell operation or by the laser treatment itself, which could not have been correctly applied. When analysing the EDX image for this modified GDL (Figure 12c), it can be observed that the pattern appears to be irregular throughout the sample and the lines are not clearly visible, suggesting that the pathways were not hydrophilic enough in this structure, impeding the correct liquid water transport through them.

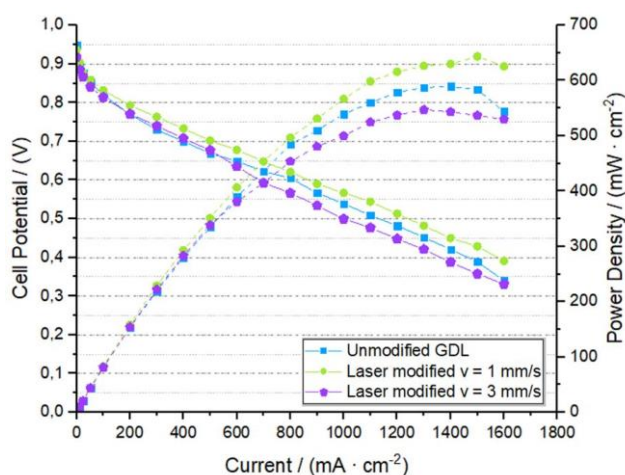


Figure 16 - Polarization and Power Density curves for 100 % RH.

Regarding the power density curve, which is obtained by multiplying the cell potential by the current, the peak power density values can be determined, normalized to the total cell area. Table 8 evidences these values, as well as the overall maximum power for the PEMFC used.

Table 8 - Peak and maximum power densities for electrochemical tests at 100 % RH.

100 % RH	Peak Power Density (mW·cm ⁻²)	Current (A)	Maximum Power (25 cm ² PEMFC) (W)
Unmodified GDL	589	35	14.7
Laser modified GDL $v=1 \text{ mm}\cdot\text{s}^{-1}$	644	37.5	16.1
Laser modified GDL $v=3 \text{ mm}\cdot\text{s}^{-1}$	547	32.5	13.7

In Figure 17 it can be visualized the polarization and power density curves for relative humidity conditions of 75 (Figure 17a) and 50 % (Figure 17b). These curves were taken only for PEMFC assembled with laser modified GDLs. To determine these curves, the temperature of the humidifiers (anode and cathode) had to be estimated: the values are based on the temperature of the cell (approximately 80 °C), and the dew point was calculated. This value corresponds to the temperature at which the gases will become saturated and, below this value, condensation will occur [27]. Thus, for 75 % RH, the dew point is approximately 73.1 °C, whereas for 50 % RH, this temperature is around 63.8 °C (values estimated considering the intended RH and the temperature of the fuel cell). It was chosen to study the polarization curves at these different RH conditions since the moisture of the reactant gases, in the humidifiers, has a great influence on water management and, consequently, on the performance of the PEMFC.

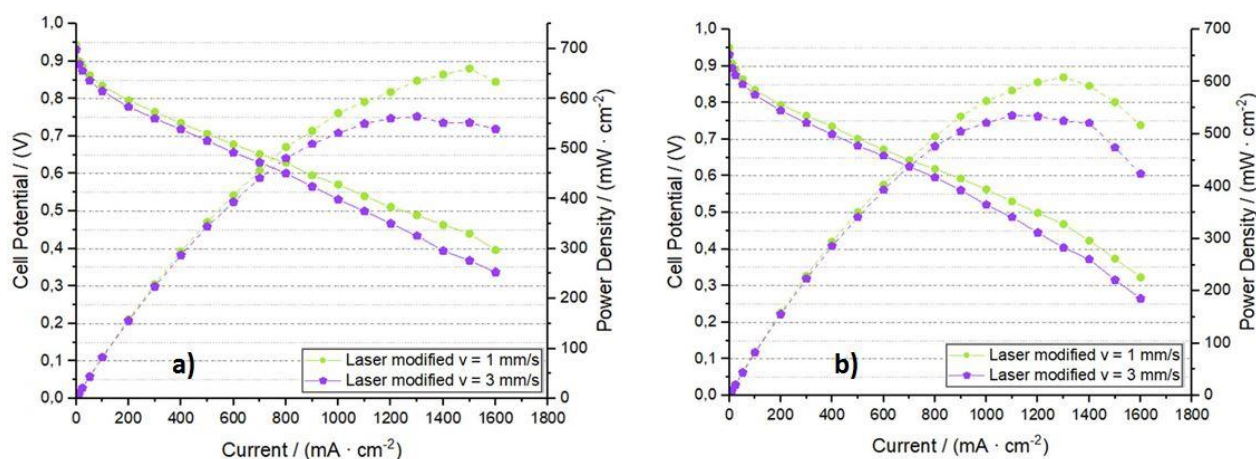


Figure 17 - Polarization and Power Density curves for 75 % RH (a) and 50 % RH (b).

The potential losses, intrinsic to the polarization curves, can be explained by the degradation of the membrane (loss of proton conductivity) or even of the GDL, due to carbon corrosion, affecting the transport of reactants. Nevertheless, and as expected, the laser treatment with the lowest driving speed ($1 \text{ mm}\cdot\text{s}^{-1}$) resulted in better results for the overall performance of the cell. With these measurements, it can be reinforced the viability of the laser modification

as a promising technique for future developments. Tables 25 and 26 in Appendix 2 reveal the peak and maximum power densities for the remaining RH conditions. By the comparison between all values obtained, it can be concluded that not only the performance is greater when the PEMFC is assembled with the laser modified GDL, treated with laser speed of $1 \text{ mm} \cdot \text{s}^{-1}$, but also that this performance achieves its greatest value for 75 % RH (peak power of $660 \text{ mW} \cdot \text{cm}^{-2}$).

Figure 18 provides a chart of the peak power densities, where it can be observed the conclusions taken above, highlighting the best result obtained. Thereby, a good overall performance can be reached providing less energy to the system because the temperature of the humidifiers is lower than when operating at maximum humidity conditions. Approximating to a real system, this is a good indicator that the modification technique applied has advantages and should be develop further.

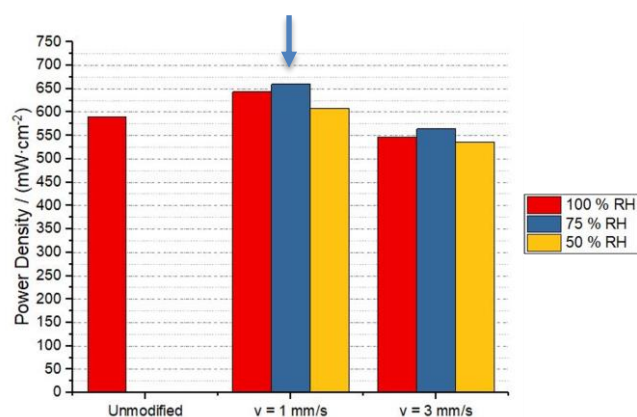


Figure 18 - Peak power densities for the different modified MPLs.

A different approach could be also analysed in this topic: instead of comparing the fuel cells assembled with different GDLs at the cathode side, compare, for the same PEMFC, the different relative humidity conditions applied. Figure 19 evidences the polarization and power density curves for the PEMFC assembled with a laser modified GDL at laser velocity speed $1 \text{ mm} \cdot \text{s}^{-1}$ (Figure 19a) and laser speed $3 \text{ mm} \cdot \text{s}^{-1}$ (Figure 19b).

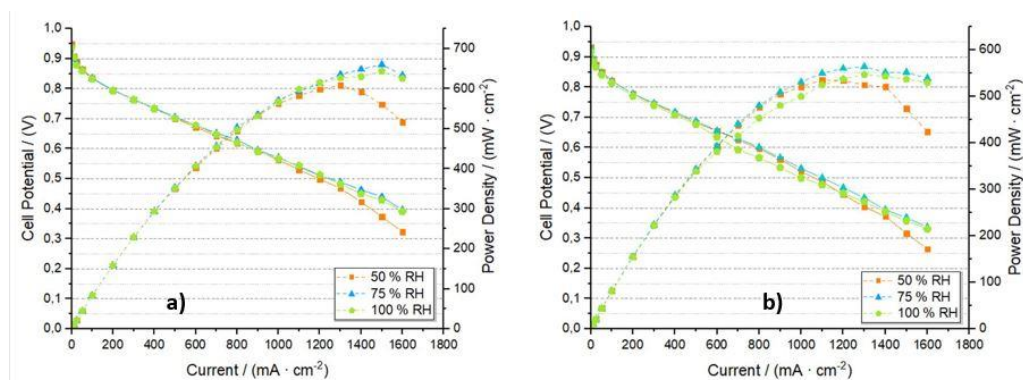


Figure 19 - Polarization and Power Density curves for a laser modified GDL $v=1 \text{ mm} \cdot \text{s}^{-1}$ (a) and $v=3 \text{ mm} \cdot \text{s}^{-1}$ (b).

Indeed, both cells tested in this experimental part achieved better results when operating at 75 % RH, leading to a better system optimization, as mentioned above.

Table 9 states some cell potential values for the three distinct regions identified in a polarization curve: the activation polarization (identified by number 1 in the table), the ohmic polarization (number 2) and the concentration polarization (number 3) region. This table is related to relative humidity conditions of 75 %, which were the best results obtained in this part of the work. In addition, it provides information about the Open Circuit Potential (OCP) for the PEMFCs, which is the value obtained when the cell is exposed to low or zero current conditions. Tables 27 and 28 in Appendix 2 demonstrate the same information presented below, for relative humidity of 100 and 50 %, respectively.

Table 9 - Values of the current for the different polarization regions at 75 % RH.

RH	Region	Laser modified $v=1 \text{ mm}\cdot\text{s}^{-1}$		Laser modified $v=3 \text{ mm}\cdot\text{s}^{-1}$	
		Current ($\text{mA}\cdot\text{cm}^{-2}$)	Cell Potential (V)	Current ($\text{mA}\cdot\text{cm}^{-2}$)	Cell Potential (V)
75 %	1	300	0.764	300	0.747
	2	600	0.678	600	0.656
	3	1 500	0.440	1 500	0.368
OCP (V)		0.953		0.910	

In addition to the polarization curves, other electrochemical methods could have been used, for example, the EIS. This *in-situ* method is important because it allows the monitoring of the fuel cells' health and a more efficient control of the system [22]. This way, parameters like membrane resistance and mass/charge transfers are better controlled. CV is another method that can be carried out to study the effects of contaminants on the overall performance of the cell. LSV, on the other hand, allows the detection of hydrogen crossover or even any internal short circuit between the anode and the cathode [22].

4.3 Washburn method

The wettability of the laser modified GDLs corresponds to the evaluation of the internal contact angle of water, $\theta_{\text{H}_2\text{O}}$, on the inner pores of the MPL. In this experimental part of the work, the wettability was evaluated by the Washburn method.

However, the characterization of this wettability involves, firstly, the evaluation of the contact angles, θ , between the inner porous of the MPLs and a variety of different liquid solvents, selected according to specific requirements: properties such as density (ρ), surface tension (σ_{LV}) and dynamic viscosity (μ) of the liquids must be known in order to apply the Washburn equation (Equation 2.4).

Thereby, the laser modified MPLs, as well as unmodified ones were submitted to these experiments and the internal contact angles were estimated for different liquids, towards the final objective of this work, the extrapolation to water: $\theta_{\text{H}_2\text{O}}$. The experiments passed by measuring the mass uptake along time, firstly of the GDLs with a reference solvent and then with the remaining liquids. The data referred to the reference solvent is used to estimate the Washburn constant, C_W , which remains the same for the whole set of experiments and is required for the determination of the contact angles with the other solvents. All the measurements were practically made at room temperature and at least two sets of experiments were run, for each solvent, to make sure the data was reproducible.

The choice of an adequate reference solvent was made according to the surface tension and viscosity values, which should be low, to be able to assume a perfect wettability (null contact angle). Preferentially, it should be a short straight-chain alkane (such as n-pentane, n-hexane or n-octane) with negligible evaporation. With these conditions satisfied, a good estimation of C_W is possible.

The Washburn experiments were performed with the test liquids listed in Table 10, since their surface tensions and other important properties, at specific temperatures, are well known.

Table 10 - Useful properties of the solvents used in the Washburn experiments [28], [29].

Solvent	ρ @ 20 °C (kg·m ⁻³)	σ_{LV} @ 25 °C (N·m ⁻¹)	μ @ 25 °C (Pa·s ⁻¹)
n-octane	702.5	2.114×10^{-2}	5.2×10^{-4}
n-hexane	660	1.789×10^{-2}	3.3×10^{-4}
n-heptane	680	1.965×10^{-2}	3.8×10^{-4}
DMSO	1 100	4.292×10^{-2}	2.5×10^{-3} (*)
THF	890	2.668×10^{-2}	5.3×10^{-4}
Ethylene glycol	1 113	4.799×10^{-2}	1.7×10^{-2}
Glycerol	1 260	6.340×10^{-2}	9.5×10^{-1}
1,4-dioxane	1 030	3.275×10^{-2}	1×10^{-5}
o-xylene	880.1	2.976×10^{-2}	7.6×10^{-4}
Toluene	870	2.793×10^{-2}	5.6×10^{-4}

(*) dynamic viscosity @ 20 °C

Three sets of experiments were performed towards the optimization of the combination reference solvent/liquid tests. Therefore, the experiments were performed with n-octane, n-hexane and n-heptane as reference solvents and the remaining liquids presented in the table as test solvents (see Table 3 for more detailed description of the experiments carried out).

The following subsections analyse and discuss the results obtained under the light of the Washburn approach.

4.3.1 Washburn experiments with n-octane as reference solvent

n-octane (C_8H_{18}) is a non-polar molecule since the difference in electronegativity between C and H is lower than 0.5 (according to the Pauling scale, [33]). In addition, its surface tension and dynamic viscosity values (Table 10) are low and can be considered, therefore, a reference solvent for the Washburn experiments. This way, it is assumed that this solvent will completely wet the samples and thus its contact angle is null.

Figure 20 provides a good comparison of the mass uptake for different structured samples. In Figure 21, it is observed the m^2 vs. t plot for the reference solvent. The sudden jump observed in this plot (within the first few seconds after the beginning of the measurements) corresponds to the moment at which the sample enters in contact with the surface of the liquid and the gain, in mass, starts to increase. The plots for the different structures are identified by the different colours in the figure. The expected plot for this first part would be a larger mass gain for all the laser modified samples, when compared to the unmodified. This because the laser treatment aimed to enhance the hydrophilic properties of the structure and, therefore, the liquids could rise within the sample through the new pathways created.

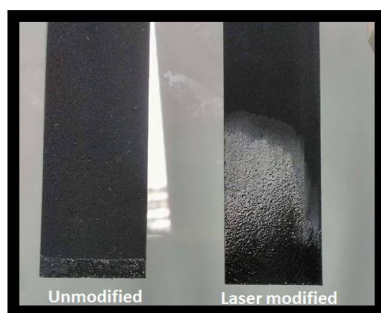


Figure 20 - Comparison between an unmodified and a laser modified ($v=1 \text{ mm}\cdot\text{s}^{-1}$) GDL for THF.

However, for the modified samples at laser processing speeds 3 and $5 \text{ mm}\cdot\text{s}^{-1}$, this did not occur, and the mass gain demonstrated to be lower than the one for the unmodified GDL. Nevertheless, for laser process speed of $1 \text{ mm}\cdot\text{s}^{-1}$, which is the modified structure that lead to most promising results until this point of the work, was the one which absorbed better the reference solvent, as well as the laser modified at processing speed of $10 \text{ mm}\cdot\text{s}^{-1}$.

For the test liquid solvents in this first set of experiments (DMSO, THF, 1,4-dioxane, o-xylene, toluene, glycerol and ethylene glycol) the same record of experimental data was carried out and the corresponding plots for the evolution gain, in mass, can be found in Appendix 3 (Figures 30 to 36).

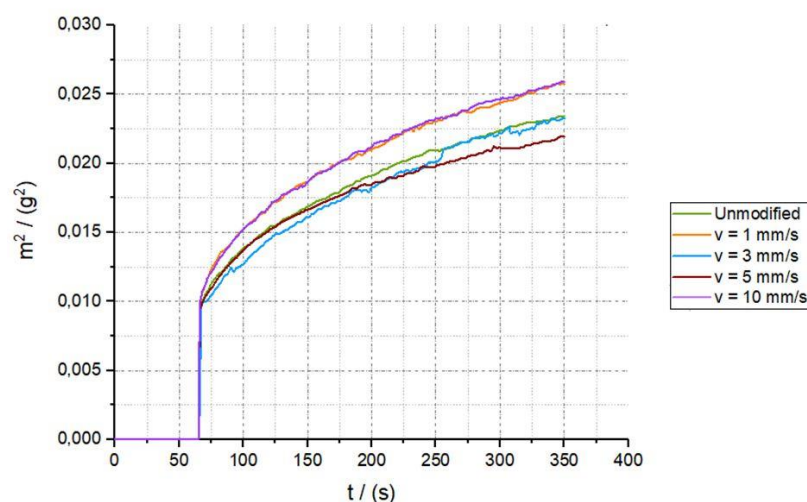


Figure 21 - Time evolution of the gain, in mass, for *n*-octane.

From the analysis of the graphs, it can be observed that for the specific cases of DMSO, ethylene glycol and glycerol, the shape of the plot differs from the remaining ones: the mass uptake rapidly decreased (reaching negative values) the moment that the surface of the GDL entered in contact with them. These three solvents have the highest density of all the used test solvents (see Table 10), which can explain this behaviour and indicates that none of the solvents were absorbed. Thereby, when repeating the experiments, a new approach was attempted: instead of just touching the surface of the liquid, the GDL was immersed into the liquid for about 1 cm of its total length and only then the measurements started. However, the same behaviour was observed, leading to the same conclusions as mentioned above.

Comparing all the mass uptake graphs, it can also be observed that the rate of solvent imbibition is not the same for all the solvents. When this rate is significantly lower than the other ones, it can be an indicator that a significant evaporation occurred during solvent imbibition (leading to the foresight of the full saturation of the sample). On the other hand, greater slopes of the m^2 vs. t curves, within the first few seconds, implies that the liquids advanced faster in the sample and could be a synonym of good wettability of the inner surfaces of the GDL. Furthermore, it implies that the penetration rate is heavily dependent on the properties of the liquid, due to the interaction between the pore walls and the intermolecular forces that pull the liquid upward. Applying this to the obtained curves, it can be assumed that the rate of penetration will decrease as higher is the density, surface tension or viscosity of the liquid.

Figure 22 evidences the slow rate of penetration for one of the mentioned solvents: glycerol. In the image it can be then confirmed that this solvent, which has the higher density, surface tension and viscosity, was not absorbed well by the GDL and that, probably, its contact angle cannot be determined.

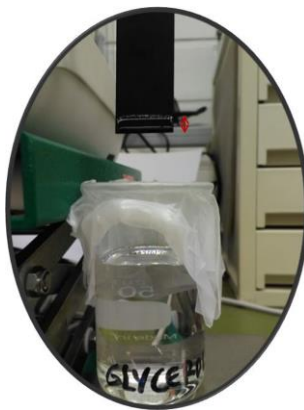


Figure 22 - Mass uptake for glycerol (unmodified MPL).

The measurements that took place in this work lasted for about 7 minutes each; they were left to stabilize for about 5 minutes and no longer since the relevant data for the determination of the contact angles is obtained right at the beginning of the experiment - the jump and initial mass uptake observed for all the plots.

For the application of the Washburn method (Equation 2.4), the Washburn constant needs to be estimated to the reference solvent that is being used, in this case, *n*-octane. Evidences in the literature show that, when applying this method, a more reasonable contact angle can be obtained by using only the linear penetration rate profile at the beginning of the penetration process [30]. Thus, it only depends on the initial slope of the mass uptake curves: $\frac{m^2}{t}$, since that the remaining parcels of the equation are already known (as it refers to the reference solvent, the contact angle value is null, and thus $\cos \theta = 1$ and the properties of the liquid are listed in Table 10). With the aid of the Origin® Graphing & Analysis software, the slopes were analysed in careful detail. This part of the calculations presents some disadvantages and is not too precise, requiring greater attention: there is no accurate method to evaluate these initial slopes and its determination depends only on the perspective of who is analysing them.

In Figure 23 it can be observed, for the case where *n*-octane was tested, the amplification of these initial slopes, with the aid of Origin®. The slopes needed to be determined for each different sample analysed, leading to five different values of the Washburn constant and, consequently, to five different θ_{H_2O} , for each group. The evaluation of these slopes was as precise as possible, with the values obtained corresponding to the moment when the sudden jump appears in the graph.

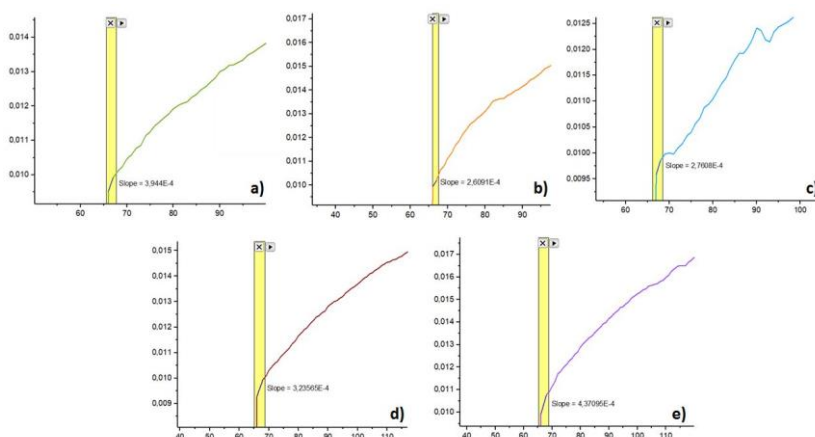


Figure 23 - Determined slopes for unmodified (a) and laser modified GDLs velocities 1 (b), 3 (c), 5 (d) and 10 (e) $\text{mm}\cdot\text{s}^{-1}$ (Origin®) for n-octane.

Equation (2.10) shows a calculus example of how C_W was determined, through the Washburn equation and for the unmodified GDL. Table 11 evidences all the evaluated Washburn constants for the first set of the Washburn experiments.

$$\frac{m^2}{t} = \frac{C_W \cdot \rho^2 \cdot \sigma_{LV} \cdot \cos \theta}{\mu} \Rightarrow 3.944 \cdot 10^{-4} = \frac{C_W \cdot 702.5^2 \cdot 2.114 \cdot 10^{-2} \cdot \cos(0)}{5.2 \cdot 10^{-4}} \quad (2.10)$$

Table 11 - Evaluation of the Washburn constants for n-octane as reference solvent.

Sample	C_W
Unmodified GDL	1.947×10^{-17}
Laser modified GDL $v=1 \text{ mm}\cdot\text{s}^{-1}$	1.288×10^{-17}
Laser modified GDL $v=3 \text{ mm}\cdot\text{s}^{-1}$	1.363×10^{-17}
Laser modified GDL $v=5 \text{ mm}\cdot\text{s}^{-1}$	1.598×10^{-17}
Laser modified GDL $v=10 \text{ mm}\cdot\text{s}^{-1}$	2.158×10^{-17}

It can be observed that the value of C_W decreases when passing from a GDL that did not suffer from any laser treatment to a laser modified one; also, within the laser modified ones, this value increases when passing from a lower to a greater laser velocity speed. Taking a closer look at the values of the slopes in Figure 23 and to Equation (2.10), it can be concluded that greater slopes (unmodified GDL) imply greater value of C_W , and vice-versa. In addition, the slope increases with the laser velocity speed applied, and thus C_W is greater for the highest velocity speeds. All of this is in consonance with the Washburn equation and the laser modified MPL at velocity $1 \text{ mm}\cdot\text{s}^{-1}$ continues to follow expectations, confirmed by the good results associated with this structure.

With the value of C_W determined, for each group of tested samples, the evaluation of the rest of the slopes, for each solvent used (DMSO, THF, 1,4-dioxane, o-xylene, toluene, glycerol e ethylene glycol) and for each structured sample was estimated. This approach was carried out as it was for n-octane: using the amplification of the squared mass uptake curves for every

plot recorded and, with the aid of Origin®, the slopes were estimated. Applying, again, the Washburn equation (now with the values of C_w known), the contact angles (θ) for each liquid solvent could be estimated. Table 12 presents all the determined contact angles, for each group of samples.

This table does not include glycerol, since the contact angle for this liquid solvent could not be estimated, as previously said. Ethylene glycol is the second liquid with the highest viscosity, as well as surface tension and density values. Therefore, its rate of penetration was smaller when compared to the other solvents. This behaviour can be observed by the mass uptake for this liquid, presented in Figure 22, where the mass rapidly decreased the moment that the samples touched its surface, indicating that it was not well absorbed. However, two contact angles could be estimated, despite these assumptions.

Table 12 - Resume of the contact angles, determined for n-octane as reference solvent.

	Solvent	Unmodified GDL	Laser modified GDL	Laser modified GDL	Laser modified GDL	Laser modified GDL
			$v=1 \text{ mm}\cdot\text{s}^{-1}$	$v=3 \text{ mm}\cdot\text{s}^{-1}$	$v=5 \text{ mm}\cdot\text{s}^{-1}$	$v=10 \text{ mm}\cdot\text{s}^{-1}$
Contact angle θ (°)	n-octane	0	0	0	0	0
	DMSO	98.56	95.48	77.70	87.78	84.17
	THF	77.07	68.64	79.52	78.03	84.03
	Ethylene glycol	51.19	112.92	-	-	-
	1,4-dioxane	89.98	89.93	89.98	89.88	89.91
	o-xylene	79.44	56.64	78.58	82.73	86.88
	Toluene	81.99	30.09	65.89	42.26	88.66

Contact angles below 90° indicate a high wettability (more hydrophilic surface), and the contrary is observed for contact angles above 90° (more hydrophobic surface). With more hydrophilic surfaces, the interaction between the liquid and them is stronger. The time required to reach equilibrium is greater in these cases, since it is the time for the liquid molecules to spread/cover the surface (this behaviour was not observed for all graphs since the time for stabilization was not an objective in this part of the work). For hydrophobic polymers the contrary is observed.

Thus, from the analysis of Table 12, it can be concluded that, except for DMSO and ethylene glycol, all the liquid tested solvents provided good wettability. Toluene demonstrated to be the solvent providing the best hydrophilic characteristics to the surface, wetting almost completely the sample.

Finally, with all the data carefully analysed, the Zisman plots can be set, allowing the extrapolation to water. Figure 24 evidences the Zisman plot for the laser modified GDL at speed $1 \text{ mm}\cdot\text{s}^{-1}$ (see Figures 37 to 40 in Appendix 3 for the remaining structured samples).

This type of plot considers the cosine of the determined contact angles for the liquids, and their surface tension. The reference solvent is standing out in the plot, by a horizontal line, as the one to have perfect wettability and the remaining wetting fluids by different colours.

From the analysis of Figure 24, it can be observed a tendency for the contact angle to decrease (the cosine increases) as the surface tension decreases. This can also be observed for all the Zisman plots elaborated, for each structured sample.

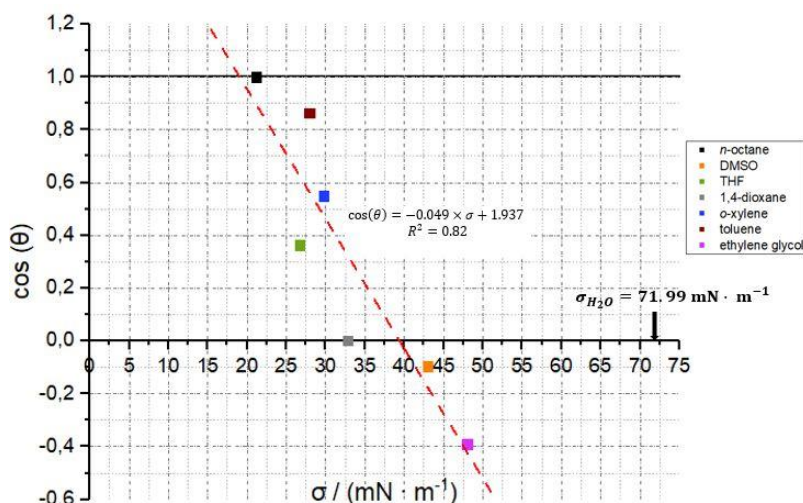


Figure 24 - Zisman plot for laser modified GDL $v=1 \text{ mm}\cdot\text{s}^{-1}$ (n-octane as reference solvent).

Better adjustments of this plot were obtained for the laser modified MPL at laser velocity speed of $1 \text{ mm}\cdot\text{s}^{-1}$; thus, it is continued to be demonstrated, and validated, the importance of this structured GDL for future use.

A fair approximation to water is made by the linear fit of the plot and $\theta_{\text{H}_2\text{O}}$ can be extrapolated, since the surface tension of water is a known value. Table 13 evidences the final values obtained with the Washburn method, for water.

Table 13 - Extrapolation to water (from the Zisman plots) for n-octane as reference solvent.

n-octane reference solvent	$\cos \theta_{\text{H}_2\text{O}}$	$\theta_{\text{H}_2\text{O}} (^{\circ})$
Unmodified GDL	-0.157	99.02
Laser modified GDL $v=1 \text{ mm}\cdot\text{s}^{-1}$	-1.601	-
Laser modified GDL $v=3 \text{ mm}\cdot\text{s}^{-1}$	-0.913	155.94
Laser modified GDL $v=5 \text{ mm}\cdot\text{s}^{-1}$	-1.366	-
Laser modified GDL $v=10 \text{ mm}\cdot\text{s}^{-1}$	-1.064	-

Values of the cosine are also presented in this table because, as can be observed, it is not always possible to extrapolate the supposed contact angle between a GDL and water. This indicates that either the reference solvent was not suitable for these experiments and, thus,

should be changed; or the list of the remaining liquid tests was also not suitable for these experiments and requires change too. Another possibility relates to the fact that, in these experiments, the balance used to record the mass uptake was too sensible to outside perturbations, leading to an imprecise plot and consequently, an imprecise analysis of the initial slope.

Taking in consideration these possibilities, it was firstly decided that the reference solvent should change, maintaining the rest of the conditions. Thereby, two more sets of experiments were carried out, the same way as for n-octane and leading to different results. Since the approach is the same for the following two sets of experiments, only the most important information will be presented next.

4.3.2 Washburn experiments with n-hexane as reference solvent

n-hexane (C_6H_{14}) was chosen as the second reference solvent for this second set of Washburn experiments, alongside with DMSO, THF, 1,4-dioxane, o-xylene, toluene, glycerol and ethylene glycol as the remaining liquid tests. It is also a non-polar molecule and, given its main properties presented in Table 10, can be considered as perfectly wetting the samples (and thus, the contact angle is null).

In Appendix 3, Figure 41 represents the squared mass uptake for the reference solvent and Figure 42 the amplification of the initial slopes which lead to the determination of the Washburn constants for the different structured samples. These values are represented in Table 29. For the values in this set, the results did not occur as expected, since the C_W increased when passing from the unmodified to the laser modified structures. In addition, there is no tendency within the laser modified ones, where the value of this constant should increase from lower to higher velocity laser speeds. Errors committed in this part of the experimental work include, as previously said, the inaccurate evaluation of the slopes, which is made by eye and therefore there is no exact point where these data should be retrieved; also, the Washburn experiment itself, due to instability of the balance used and thus the data could be not be viable enough to apply this method.

Table 30 in Appendix 3 displays the contact angles obtained for the different liquids, through the Washburn equation. Ethylene glycol could only be estimated for the lasered-treated sample at velocity $1 \text{ mm}\cdot\text{s}^{-1}$ and not for all of them, for the same reasons already mentioned. In addition, glycerol had to be excluded from the calculations, since it was not absorbed by the samples. In general, the solvents provided good wettability.

Figure 25 presents the Zisman plot for the laser modified MPL (laser speed $1 \text{ mm}\cdot\text{s}^{-1}$), while Figures 43 to 46, in Appendix 3, the Zisman plots for the other structured samples. Better results were obtained for the laser modified GDL at velocity $1 \text{ mm}\cdot\text{s}^{-1}$.

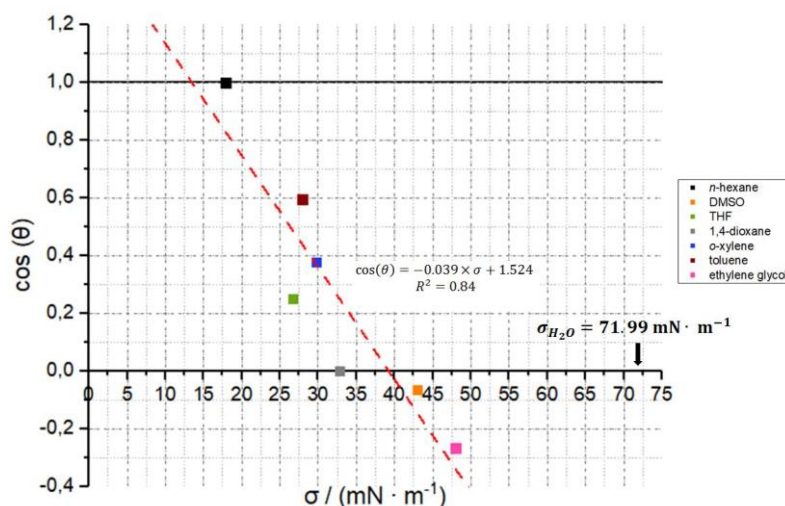


Figure 25 - Zisman plot for laser modified GDL $v=1 \text{ mm} \cdot \text{s}^{-1}$ (n-hexane as reference solvent).

Table 14 presents the final extrapolation of $\theta_{\text{H}_2\text{O}}$, when n-hexane is used as reference solvent for the Washburn experiments. Comparing with the data obtained for n-octane, even though no more additional contact angles were possible to determine, the ones estimated are smaller than the previously obtained. This implies that n-hexane is better to characterize the wettability of the inner surfaces of these modified GDLs.

Table 14 - Extrapolation to water (from the Zisman plots) for n-hexane as reference solvent.

n-hexane reference solvent	$\cos \theta_{\text{H}_2\text{O}}$	$\theta_{\text{H}_2\text{O}} (^{\circ})$
Unmodified GDL	0.374	68.03
Laser modified GDL $v=1 \text{ mm} \cdot \text{s}^{-1}$	-1.273	-
Laser modified GDL $v=3 \text{ mm} \cdot \text{s}^{-1}$	-0.862	149.56
Laser modified GDL $v=5 \text{ mm} \cdot \text{s}^{-1}$	-1.201	-
Laser modified GDL $v=10 \text{ mm} \cdot \text{s}^{-1}$	-1.049	-

4.3.3 Washburn experiments with n-heptane as reference solvent

n-heptane (C_7H_{16}) was the last reference solvent tested in this part of the experimental work.

Figures 47 and 48 (see Appendix 3) represent the squared mass uptake for the reference solvent and the amplification of the initial slopes, respectively. The values of C_W for the different structured samples are represented in Table 31. As for n-hexane, the same conclusions could be withdrawn in this experiment. Table 32 (see Appendix 3) displays the contact angles obtained for the different liquids, through the Washburn equation and the same can be concluded (as for n-hexane). Figures 49 to 53 (see Appendix 3) present the Zisman plots for all the structured samples. The extrapolation for water is presented in Table 15, leading to the main conclusion that, with n-heptane as reference solvent, good wettability was not achieved.

Table 15 - Extrapolation to water (from the Zisman plots) for *n*-heptane as reference solvent.

n-heptane reference solvent	$\cos \theta_{\text{H}_2\text{O}}$	$\theta_{\text{H}_2\text{O}}$ (°)
Unmodified GDL	0.121	83.06
Laser modified GDL $v=1 \text{ mm}\cdot\text{s}^{-1}$	-1.268	-
Laser modified GDL $v=3 \text{ mm}\cdot\text{s}^{-1}$	-1.000	-
Laser modified GDL $v=5 \text{ mm}\cdot\text{s}^{-1}$	-1.351	-
Laser modified GDL $v=10 \text{ mm}\cdot\text{s}^{-1}$	-1.027	-

The Washburn method, as observed from the experiments carried out, requires special attention to ensure its viability as a characterization of wettability method. This starts right away with the preparation of the samples and the experimental facility, which should be in a non-contaminated area, since the surface of the GDLs is extremely sensitive to impurities. Constant temperature conditions are also required, since the θ strongly depends on this property.

The liquid penetration profile should also be analysed carefully, especially the initial slopes that lead to the determination of the Washburn constants. When applying this approach, it was assumed that the rest of the profile should be mostly ignored. However, whether it should be included or not, could end in different results and, thus, requires further investigation. Other error involving the determination of C_W itself was assumed to be based on just one reference solvent, which could not be the optimum one.

This process is also complex since there is not an “universal” list of liquids recommended for testing. Therefore, the decision was merely based on the surface tension values or solvents used in previous experiments.

It can be concluded, therefore, that this method is not stable enough and does not provide an accurate measure of $\theta_{\text{H}_2\text{O}}$. A new approach should be then studied.

4.4 Combination of the Washburn method with the Owens-Wendt two-parameter surface tension model

The Owens-Wendt model was combined with the Washburn method, towards a better extrapolation of $\theta_{\text{H}_2\text{O}}$. The new approach takes in consideration the polar and dispersive components of the surface tension, which is more accurate than just considering the overall value.

4.4.1 n-decane as reference solvent

The surface tension values, density and viscosity of the used test liquids are summarized in Table 16. The ratios between polar and dispersive components of the total surface tension of the liquids were calculated according to Krüss processor tensiometer database [31].

Table 16 - List of solvents and useful parameters for the Washburn experiments [31].

Solvent	ρ @ 20 °C (kg·m ⁻³)	μ @ 25 °C (Pa·s ⁻¹)	σ_{LV} @ 25 °C (N·m ⁻¹)	σ_{LV}^d (N·m ⁻¹)	σ_{LV}^p (N·m ⁻¹)
n-decane	730	8.4×10^{-4}	2.38×10^{-2}	2.38×10^{-2}	0
Cyclohexane	778.1	9×10^{-4}	2.55×10^{-2}	2.55×10^{-2}	0
n-tetradecane	762.8	2.1×10^{-3}	2.64×10^{-2}	2.64×10^{-2}	0
Toluene	862.3	5.6×10^{-4}	2.84×10^{-2}	2.61×10^{-2}	2.30×10^{-3}
Nitromethane	1 137.1	6.1×10^{-4}	3.65×10^{-2}	2.20×10^{-2}	1.45×10^{-2}
Methyl Benzoate	1 087	2×10^{-3} (*)	3.72×10^{-2}	2.70×10^{-2}	1.02×10^{-2}
Benzyl Alcohol	1 045.5	5.5×10^{-3}	3.90×10^{-2}	3.03×10^{-2}	8.70×10^{-3}
Ethylene Glycol	1 113	1.7×10^{-2}	4.77×10^{-2}	2.64×10^{-2}	2.13×10^{-2}
Diiodomethane	3 322	2.8×10^{-3} (*)	5.08×10^{-2}	5.08×10^{-2}	0
Formamide	1 133.4	3.2×10^{-3}	5.70×10^{-2}	2.24×10^{-2}	3.46×10^{-2}
Glycerol	1 261.3	9.5×10^{-1}	6.34×10^{-2}	3.70×10^{-2}	2.64×10^{-2}

(*) dynamic viscosity @ 20 °C

As this approach combines both methods, the first part (evaluation of C_w and θ for the different solvents) is developed under the light of the Washburn method. Figures 54 and 55 show the squared mass uptake for n-decane and the amplification of the parts of interest, and Table 33 the evaluation of the Washburn constants. The plots for the remaining solvents used are displayed in Figures 56 to 65. All these can be found in Appendix 3.

Table 34 (see Appendix 3) presents all the θ obtained and it can be observed that all values could be estimated, contrarily to what had been observed before with other solvents. From the analysis of this table, for nitromethane, benzyl alcohol, ethylene glycol and diiodomethane the wettability was low (θ higher than 90°), whereas the remaining solvents provided good wettability. This is a good indicative that the new list of solvents is more fit to the final extrapolation.

It is at this point that the Owens-Wendt model is taken in account. Thus, instead of a typical Zisman plot, a new one is developed regarding the components of the surface tension (Equation 2.9). Figure 26 displays it for the unmodified GDLs, whereas Figures 66 to 69 (in Appendix 3) for the remaining modified structures.

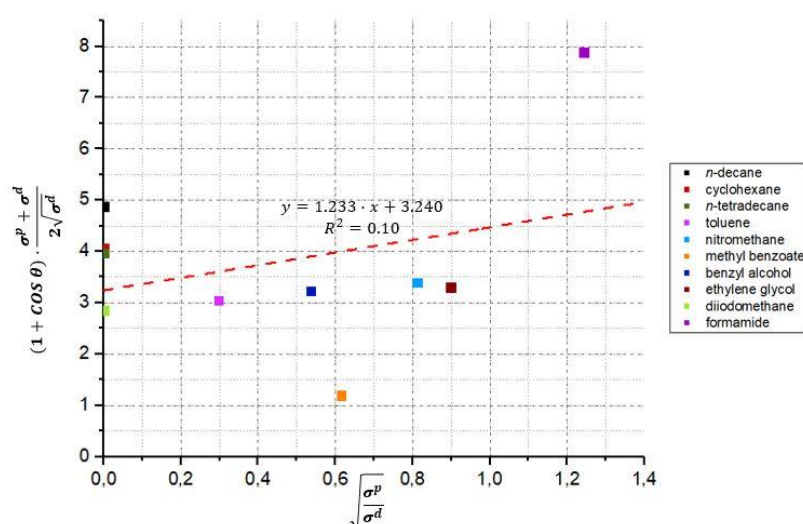


Figure 26 - Owens-Wendt two-parameter model for unmodified GDL (*n*-decane as reference solvent).

The final extrapolation to water was estimated regarding the linear regression obtained in the previous graphs and the overall surface tension of water, as well as for both components (Table 17).

Table 17 - Polar and dispersive components for the extrapolation of water.

$\sigma_{LV} @ 25\text{ }^{\circ}\text{C} \text{ (N}\cdot\text{m}^{-1}\text{)}$	$\sigma_{LV}^d \text{ (N}\cdot\text{m}^{-1}\text{)}$	$\sigma_{LV}^p \text{ (N}\cdot\text{m}^{-1}\text{)}$
7.28×10^{-2}	2.64×10^{-2}	4.64×10^{-2}

Table 18 displays, then, the extrapolated θ_{H_2O} for the different structures, when both the Washburn and the Owens-Wendt approaches are combined.

Table 18 - Extrapolation to water for *n*-decane as reference solvent, according to the Owens-Wendt model.

n-decane reference solvent	$\cos \theta_{H_2O}$	$\theta_{H_2O} (^{\circ})$
Unmodified GDL	-0.974	166.89
Laser modified GDL $v=1 \text{ mm}\cdot\text{s}^{-1}$	-0.976	167.32
Laser modified GDL $v=3 \text{ mm}\cdot\text{s}^{-1}$	-0.980	168.38
Laser modified GDL $v=5 \text{ mm}\cdot\text{s}^{-1}$	-0.974	166.99
Laser modified GDL $v=10 \text{ mm}\cdot\text{s}^{-1}$	-0.979	168.16

The values obtained indicated a strong hydrophobic surface, since θ_{H_2O} is superior to 90° . This means that the hypothesis put in the beginning of this work, which was that laser modification would possibly allow the enhancement of the hydrophilic properties of the GDLs, was not entirely proven and further investigation is required. However, the technique applied affects, somehow, the structure and wettability of the inner surfaces. The values could be

extrapolated for all the structures, contrarily to what had been observed before, indicating that the Owens-Wendt model is more precise and leads to better results. Thus, the use of the Washburn method alone is not a viable solution and a combination of this with other models should be reinforced.

Table 19 reinforces the viability of the combination of these methods: the values of $\theta_{\text{H}_2\text{O}}$ for n-heptane as reference solvent were extrapolated using this approach too, leading to more precise results.

Table 19 - Comparison between the extrapolation to water by two different approaches.

n-heptane reference solvent	$\theta_{\text{H}_2\text{O}}$ (°) (Washburn)	$\theta_{\text{H}_2\text{O}}$ (°) (Washburn and Owens-Wendt)
Unmodified GDL	83.06	68.37
Laser modified GDL $v=1 \text{ mm}\cdot\text{s}^{-1}$	-	122.02
Laser modified GDL $v=3 \text{ mm}\cdot\text{s}^{-1}$	-	104.34
Laser modified GDL $v=5 \text{ mm}\cdot\text{s}^{-1}$	-	101.65
Laser modified GDL $v=10 \text{ mm}\cdot\text{s}^{-1}$	-	112.32

5 Conclusions

The main objective of this work was to understand the effects of laser modification in the structure of a GDL. In addition, the influence of this technique in the water management, at the cathode side of a PEMFC, was also studied. Several parameters of the experimental set-up were optimized and the MPL side of the GDL was submitted to laser irradiation. The creation of hydrophilic routes for the transport of liquid water, during fuel cell operation, was the main goal here. In addition, the wettability of the inner surfaces was studied in detail, through the Washburn and the Owens-Wendt model, with the future objective of inserting new properties, such as the contact angle for water, into numerical simulation models.

It was observed, through EDX measurements, that the highest and the lowest heat impact corresponded to the lowest and highest laser speeds, respectively. Additionally, a decrease in the mass fraction of fluorine was observed, from the unmodified to the modified regions, for the laser process speed of $1 \text{ mm}\cdot\text{s}^{-1}$ and laser output power ca. 250 mW. This indicates that the laser treatment was successfully applied in this structure, with the creation of strong hydrophilic routes. For the remaining samples, the same could not be concluded and an increase in the mass fraction of fluorine was observed. The modified structures were assembled in the cathode-side of a 25 cm^2 PEMFC alongside with a CCM $0.3 \text{ mg}_{\text{Pt}}/\text{cm}^2$, with the aim of observing the effect of the laser modification in the overall performance of the fuel cell. The polarization and power density curves were taken at different relative humidity conditions and the best performance achieved corresponded to the modified structure at laser process speed of $1 \text{ mm}\cdot\text{s}^{-1}$ and with 75 % RH at the anode and cathode humidifiers. The peak power density for this cell achieved ca. $660 \text{ mW}\cdot\text{cm}^{-2}$. Compared to a conventional GDL, this modified structure showed a moderate increase in the overall performance, reinforcing the viability of the laser modification technique. In addition, it was concluded that there was no need to operate at 100 % RH conditions to achieve the greatest performance, suggesting that it is not necessary to provide so much energy for the operation of the system. The study of the wettability of the inner surfaces revealed that the use of the Washburn method to the extrapolation for water was not enough, since it resulted in inaccurate results. However, when combining this approach with the Owens-Wendt two-parameter model, the extrapolation was precise and, overall, provided good insight to the understanding of the water distribution within the GDLs. The contact angles for water were higher than 90° , concluding that, despite a more precise method was found, the structured samples remained hydrophobic and the hydrophilic properties were not enhanced as much as expected. Thus, a new approach is required, as well as some modelling support.

6 Assessment of the work done

6.1 Objectives Achieved

One of the main objectives with this work was to study the effects of the laser modification technique in the structure of the GDLs. Thereby, varying parameters such as the laser power, speed and pattern, a new modified GDL was found. When assembled to the cathode-side of the fuel cell, this modified structure achieved greater performance at 75 % RH working conditions, assuring that the water management problem was better controlled at the cathode side.

The study of the wettability of the inner surfaces of the GDLs was the second main goal in the scope of this work, to assure that the laser treatment reduced the hydrophobic properties, as far as possible. Then, a fair approximation should be made for water, predicting its behaviour, through the Zisman evaluation method. The experiments revealed that this approach was not precise enough, leading to inaccurate results. However, through a combination of both the Washburn and the Owens-Wendt model, the wettability could be predicted for all the different structures involved in this work, demonstrating that this type of approach is the one that should be reinforced in further studies. However, the results showed an unexpected behaviour of the hydrophilic properties and the abundance of fluorinated compounds, revealing that the working hypothesis needs revision.

6.2 Limitations and Future Work

The complexity of the work performed involves further investigation towards future developments in the world of fuel cells. A comparison between laser perforation of the GDLs with the technique approached in this work is encouraged, leading to the design of an optimum GDL that can be easily reproducible and implemented into industry. The electrochemical characterization of the laser modified GDL (at laser speed $1 \text{ mm}\cdot\text{s}^{-1}$, which was the one that lead to the best results) should be thorough with other methods. For instances, the use of a segmented bipolar plate, instead of a conventional one, to evaluate the current density distribution and optimize the operation. With the data collected in this work, there is room for its insertion in existing computational fluid dynamics simulations of PEMFCs, which could be improved by adding these important structural properties.

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Appendix 1

Solvents used in the Washburn experiments

For the Washburn experiments, a total of 18 solvents were handled in a controlled way, in the laboratory, considering every time the safety warnings regarding each one of them. This topic gives a brief resume of important properties, safety, management and storage details for the liquid tests used in the experiments conducted along this work.

n-octane (C_8H_{18}) is a colorless liquid with a slight odor of gasoline. It is mainly used for fuels or as a solvent (in this work, *n*-octane is one of the reference solvents in the Washburn experiments). It attacks some forms of plastics, rubber and coatings. It produces irritating vapors, it is highly flammable and causes skin and eyes irritation. In terms of storage, *n*-octane should be kept away from strong oxidants and stored in a cool place (PubChem, 2018).

n-hexane (C_6H_{14}), also used as one of the reference solvents in the Washburn experiments, is a colorless liquid with an odor of petroleum. Industrially, it is used as corrosion inhibitor and as fuel. It is mainly applied in adhesives and sealants or for paints and coatings. It is also a very volatile and flammable liquid, causing both skin and eyes irritation. *n*-hexane should be stored in a well-ventilated area and in fire-resistant containers, separated from strong oxidants (PubChem, 2018).

n-heptane (C_7H_{16}) is a colorless liquid with petroleum-like odor. Also used as a reference solvent in the Washburn experiments, this volatile liquid is used as fuel, paint or coating additive, among other uses. Is highly flammable and volatile, causing skin and eyes irritation. Thus, *n*-heptane should be stored in fireproof containers, away from strong oxidants (PubChem, 2018).

Tetrahydrofuran, or THF (C_4H_8O), is a colorless, low-viscosity liquid with an ethereal odor. It may form organic peroxides when exposed to air and attacks some forms of plastics, rubber and coatings. It is mostly used for adhesives and sealant chemicals and as solvent for many applications. It is highly flammable, causing serious eye, skin and respiratory irritation. It should only be stored when completely stabilized, in a cool, dry and well-ventilated location. In this work, is used as one of the liquid tests for the Washburn method (PubChem, 2018).

Dimethyl sulfoxide, or DMSO (C_2H_6OS), is a highly polar organic liquid, mostly used as a chemical solvent. It is a clear liquid and essentially odorless. If in contact with the skin, it can cause burning and high vapor concentrations may cause headache, dizziness and sedation. DMSO should be kept in a cool, well-ventilated area, in the dark and away from strong

oxidants (PubChem, 2018). This solvent is used in this work as a liquid solvent for the Washburn tests.

Ethylene glycol ($C_2H_6O_2$) is a colorless, odorless and viscous liquid, used in this work as a liquid solvent in the Washburn experiments. It is mainly used as an antifreeze and coolant. It can cause damage to organs after prolonged exposure, but the inhalation of its vapours is not hazardous. On combustion, ethylene glycol forms toxic gases. To a safe storage, this liquid should be separated from strong oxidants and strong bases in well-closed containers and in a dry location (PubChem, 2018).

1,4-dioxane ($C_4H_8O_2$) is another colorless liquid, with a slight ethereal odor, used as a solvent for the Washburn experiments. Exposure to high levels of this liquid can cause headaches and irritation of the eyes, nose, throat and lungs. It is also highly flammable, thus should be kept in fireproof containers, separated from strong oxidants, strong acids and incompatible materials. The containers should be kept in cool, well-ventilated locations, in the dark and 1,4-dioxane should only be stored when fully stabilized (PubChem, 2018).

Glycerol ($C_3H_8O_3$) is a clear, colorless and odorless liquid also used as a test solvent for the Washburn experiments in this work. It is highly viscous and mainly used as adsorbent and absorbent, among other industrial uses. Glycerol may cause allergic skin reaction and serious eye damage. It is not corrosive and presents little risk of ignition, being usually stored in stainless steel tanks and away from strong oxidants (PubChem, 2018).

o-xylene (C_8H_{10}) is a colorless liquid, belonging to the family of toluenes. In terms of corrosivity, it has no reaction with common materials. It is highly flammable and harmful when in contact with skin and eyes. For a safe storage, o-xylene should be separated from strong oxidants and strong acids, in fireproof containers (PubChem, 2018). In this work, o-xylene was also used as a liquid test for the Washburn measurements.

n-decane ($C_{10}H_{22}$) is used as a reference solvent for the performed Washburn experiments during this work. It is a colorless liquid with a characteristic odor. Mostly used as an adhesive and sealant, fuels or other related products, n-decane is highly flammable. Thus, it should be kept in fireproof and cool containers, in a dry and well-ventilated location (PubChem, 2018).

Cyclohexane (C_6H_{12}) is another of the liquid tests involved in the Washburn experiments performed in this work. It is mainly used for agricultural purposes, as corrosion inhibitor, as fuel, lubricant, among many others. It is highly flammable and can cause skin irritation. Cyclohexane should be stored in an area without drain or sewer access, in fireproof containers (PubChem, 2018).

n-tetradecane ($C_{14}H_{30}$) is a colorless liquid, used as test solvent for the Washburn experiments. It is mainly used as fuel, or fuel additive, as lubricant, among other industrial

uses. It may be fatal if swallowed and its vapours are irritating to the eyes and skin. To a safe storage, the containers should be kept tightly closed in a dry and well-ventilated location. Since n-tetradecane is a combustible liquid, the containers which are opened must be carefully released and kept upright to prevent leakage (PubChem, 2018).

Toluene (C_7H_8) was used as a liquid test for the Washburn experiments carried out in this work. It is a colorless liquid with a benzene-like odor. The major use of toluene is a mixture, added to gasoline, to improve octane ratings. It is also used to produce benzene and as a solvent in paints, coatings, among others. It is highly flammable, causing skin irritation and damage to organs in cases of long exposure. Toluene is non-corrosive, but it should be stored away from strong oxidants and in fireproof containers (PubChem, 2018).

Nitromethane (CH_3NO_2) is a colorless, oily, highly flammable liquid also used as a test solvent in this work. It is characterized by a strong odor and it emits toxic fumes of nitrogen oxides, upon decomposition. It is mainly used as fuel or fuel additive. In addition to be highly flammable, nitromethane can cause serious eye and organs damage and there is the risk of fire and explosion when in contact with incompatible substances. This liquid should be kept away from water sources and sewers, within fireproof containers and separated from incompatible materials (PubChem, 2018).

Methyl benzoate ($C_8H_8O_2$) is either a crystalline solid or a solid dissolved in a liquid. It is colorless and oily with a fruity odor. Thus, it is mainly used in food additives or fragrances. In this work is used as a test solvent for the Washburn experiments and it can be irritating for eyes, skin and the respiratory system. It is incompatible with strong acids, strong bases, nitrates and oxidizers. To a safe storage, the containers should be kept tightly closed in a dry and well-ventilated location (PubChem, 2018).

Benzyl alcohol (C_7H_8O) is a colorless liquid with an aromatic odor, used in this work as a liquid test for the Washburn method. In terms of corrosivity, it can attack some forms of plastics and its main uses include agricultural chemicals, adhesives and sealants; among others. Benzyl alcohol is harmful in contact with the skin and can cause serious eye irritation. It should be stored in stainless steel tanks and its surface should be covered with nitrogen, due to its rapid oxidation (PubChem, 2018).

Diiodomethane (CH_2I_2) is harmful when in contact with both skin and eyes. It may also cause respiratory irritation (PubChem, 2018). The containers for the safe storage of diiodomethane should be kept tightly closed, protected from the light and in dry, well-ventilated places. Diiodomethane, like for this experimental work, is widely used as a test liquid for evaluation of the polar and dispersive components of the surface energy (Merck Millipore, 2018).

Formamide (CH_3NO) is a colorless, oily and viscous liquid with a slight odor of ammonia. It is mostly used as corrosion inhibitor and lubricant. It is suspected of causing cancer and of causing damage to the organs after repeated exposure. Formamide can attack copper, brass and even lead; thus, it should be kept away from oxidants, acids and bases, in stainless steel or aluminium tanks (PubChem, 2018).

Table 20 resumes all the main properties of the solvents used in the Washburn experiments. Other properties like density, viscosity and surface tension are required for the calculations in this work and were therefore previously presented.

Table 20 - Resume of the main properties of all the solvents used in the Washburn method.

Solvent	Molecular formula	Formula weight ($\text{g} \cdot \text{mol}^{-1}$)	Boiling point ($^{\circ}\text{C}$)	Melting point ($^{\circ}\text{C}$)	Vapour pressure at 20 $^{\circ}\text{C}$ (Pa)
n-octane	C_8H_{18}	114.23	125-126	-57	1400
n-hexane	C_6H_{14}	86.18	69	-94	16 000
n-heptane	C_7H_{16}	100.20	97-98	-91	4 800
n-decane	$\text{C}_{10}\text{H}_{22}$	142.29	174	-30	170*
THF	$\text{C}_4\text{H}_8\text{O}$	72.11	65	-108	19 300
DMSO	$\text{C}_2\text{H}_6\text{OS}$	78.13	189	19	59
Ethylene Glycol	$\text{C}_2\text{H}_6\text{O}_2$	62.07	195-198	-13	7
1,4-dioxane	$\text{C}_4\text{H}_8\text{O}_2$	88.11	101	12	3 900
Glycerol	$\text{C}_3\text{H}_8\text{O}_3$	92.09	290	19	0.01*
o-xylene	C_8H_{10}	106.17	143-145	-25	700
Cyclohexane	C_6H_{12}	84.16	81	6	10 300
n-tetradecane	$\text{C}_{14}\text{H}_{30}$	198.39	254	6	1.55*
Toluene	C_7H_8	92.14	111	-95	3 800*
Nitromethane	CH_3NO_2	61.04	101	-29	3 700
Methyl benzoate	$\text{C}_8\text{H}_8\text{O}_2$	136.15	199	-12	50.66*
Benzyl alcohol	$\text{C}_7\text{H}_8\text{O}$	108.14	205	-15	13
Diiodomethane	CH_2I_2	267.84	181	6	113
Formamide	CH_3NO	45.04	211	3	8

*vapour pressure at 25 $^{\circ}\text{C}$

Conditioning test for the electrochemical characterization

Table 21 presents the anode and cathode flows applied, as well as values for the current, for the condition test of the fuel cell. This test lasts for about 3 hours and it is important for the cell to adapt to the defined conditions, before the polarization curves take place.

Table 21 - Operating conditions for the conditioning test.

Anode Flow (mL)	Cathode Flow (mL)	Current (A)	Anode Flow (mL)	Cathode Flow (mL)	Current (A)
70	180	0	189	597	17.5
70	180	0.3	215	680	20
70	180	0.6	241	763	22.5
70	180	1.3	267	846	25
70	180	2.5	293	929	27.5
70	180	5	319	1013	30
84	265	7.5	345	1104	32.5
115	350	10	375	1179	35
136	431	12.5	398	1263	37.5
162	514	15	424	1345	40

Appendix 2

Physical characterization of the laser modified GDLs: EDX measurements

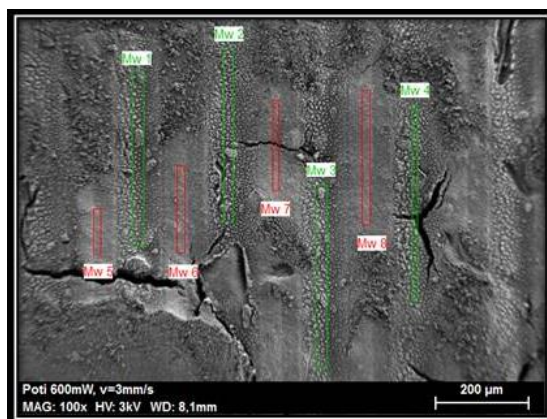


Figure 27 - Laser modified GDL ($v=3 \text{ mm}\cdot\text{s}^{-1}$) for mass fraction analysis.

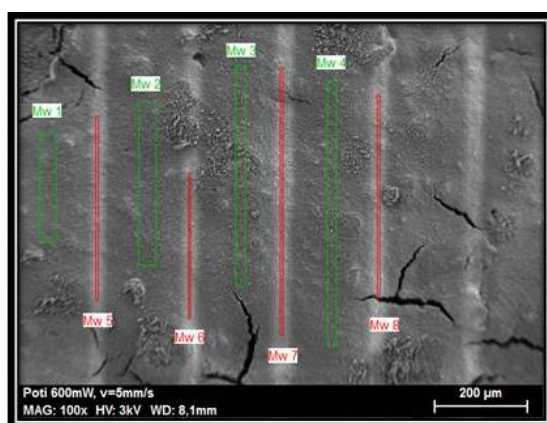


Figure 28 - Laser modified GDL ($v=5 \text{ mm}\cdot\text{s}^{-1}$) for mass fraction analysis.

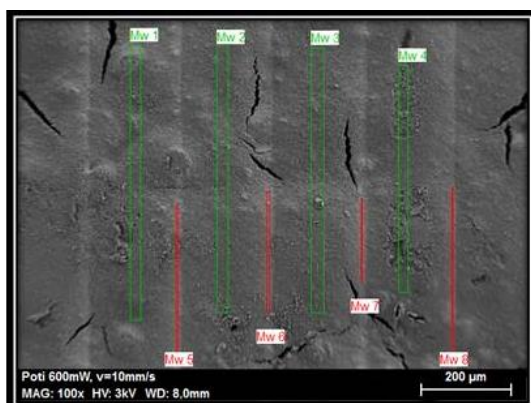


Figure 29 - Laser modified GDL ($v=10 \text{ mm}\cdot\text{s}^{-1}$) for mass fraction analysis.

Table 22 - EDX measurements: mass fraction for laser modified GDL $v=3 \text{ mm}\cdot\text{s}^{-1}$.

Region	C	O	F	Region	C	O	F	Na
Mw 1	92.33	1.61	6.06	Mw 5	90.27	0.66	7.48	0.89
Mw 2	91.37	2.11	6.52	Mw 6	88.29	0.73	9.36	1.62
Mw 3	91.93	1.47	6.60	Mw 7	89.44	0.61	7.72	2.22
Mw 4	92.40	1.80	5.80	Mw 8	89.47	1.14	8.02	1.36

Table 23 - EDX measurements: mass fraction for laser modified MPL $v=5 \text{ mm}\cdot\text{s}^{-1}$.

Region	C	O	F	Region	C	O	F	Na
Mw 1	94.70	2.24	3.05	Mw 5	78.83	0.92	19.41	0.84
Mw 2	95.82	1.97	2.21	Mw 6	81.55	0.88	16.56	1.01
Mw 3	95.05	2.20	2.75	Mw 7	79.40	0.64	19.12	0.84
Mw 4	95.96	1.91	2.12	Mw 8	78.78	0.91	19.46	0.85

Table 24 - EDX measurements: mass fraction for laser modified MPL $v=10 \text{ mm}\cdot\text{s}^{-1}$.

Region	C	O	F	Region	C	O	F	Na
Mw 1	97.68	0.97	1.35	Mw 5	90.10	0.89	7.10	1.92
Mw 2	97.07	0.97	1.96	Mw 6	91.30	0.59	5.92	2.18
Mw 3	97.44	1.05	1.52	Mw 7	89.31	1.01	7.30	2.37
Mw 4	98.09	0.77	1.14	Mw 8	91.71	0.74	5.05	2.50

Electrochemical characterization of the laser modified GDLs

Table 25 - Peak and maximum power densities for electrochemical tests at 75 % RH.

75 % RH	Peak Power Density ($\text{mW}\cdot\text{cm}^{-2}$)	Current (A)	Maximum Power (25 cm^2 PEMFC) (W)
Laser modified GDL $v=1 \text{ mm}\cdot\text{s}^{-1}$	660	37.5	16.5
Laser modified GDL $v=3 \text{ mm}\cdot\text{s}^{-1}$	564.2	32.5	14.1

Table 26 - Peak and maximum power densities for electrochemical tests at 50 % RH.

50 % RH	Peak Power Density ($\text{mW}\cdot\text{cm}^{-2}$)	Current (A)	Maximum Power (25 cm^2 PEMFC) (W)
Laser modified GDL $v=1 \text{ mm}\cdot\text{s}^{-1}$	608.4	32.5	15.2
Laser modified GDL $v=3 \text{ mm}\cdot\text{s}^{-1}$	535.7	27.5	13.4

Table 27 - Values of the current for the different polarization regions at 100 % RH.

RH	Region	Unmodified		Laser modified $v=1 \text{ mm}\cdot\text{s}^{-1}$		Laser modified $v=3 \text{ mm}\cdot\text{s}^{-1}$	
		Current ($\text{mA}\cdot\text{cm}^{-2}$)	Cell Potential (V)	Current ($\text{mA}\cdot\text{cm}^{-2}$)	Cell Potential (V)	Current ($\text{mA}\cdot\text{cm}^{-2}$)	Cell Potential (V)
100 %	1	300	0.730	300	0.763	300	0.740
	2	600	0.649	600	0.678	600	0.635
	3	1 500	0.389	1 500	0.429	1 500	0.358
OCP (V)		0.950		0.953		0.910	

Table 28 - Values of the current for the different polarization regions at 50 % RH.

RH	Region	Laser modified $v=1 \text{ mm}\cdot\text{s}^{-1}$		Laser modified $v=3 \text{ mm}\cdot\text{s}^{-1}$	
		Current ($\text{mA}\cdot\text{cm}^{-2}$)	Cell Potential (V)	Current ($\text{mA}\cdot\text{cm}^{-2}$)	Cell Potential (V)
50 %	1	300	0.764	300	0.745
	2	600	0.672	600	0.655
	3	1 500	0.374	1 500	0.316
OCP (V)		0.953		0.910	

Appendix 3

Results and discussion regarding the Washburn experiments

- n-octane as reference solvent (1st set of experiments)

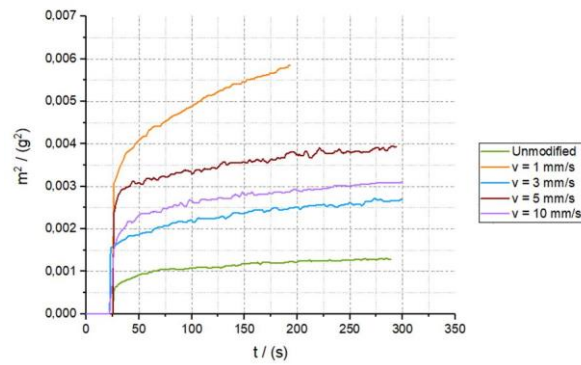


Figure 30 - Time evolution of the gain, in mass, for 1,4-dioxane.

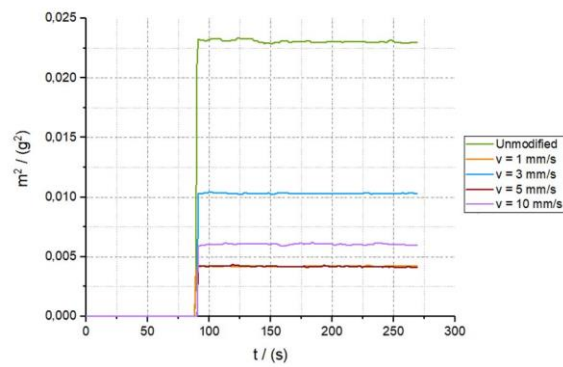


Figure 31 - Time evolution of the gain, in mass, for DMSO.

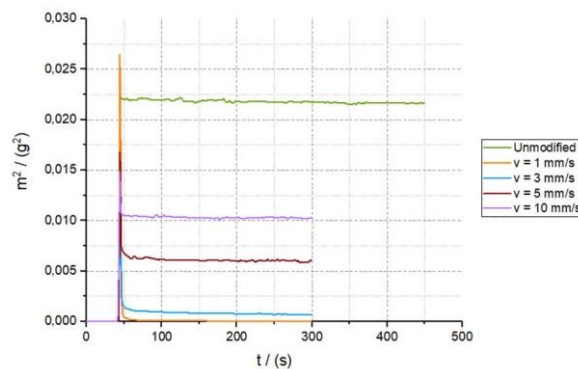


Figure 32 - Time evolution of the gain, in mass, for ethylene glycol.

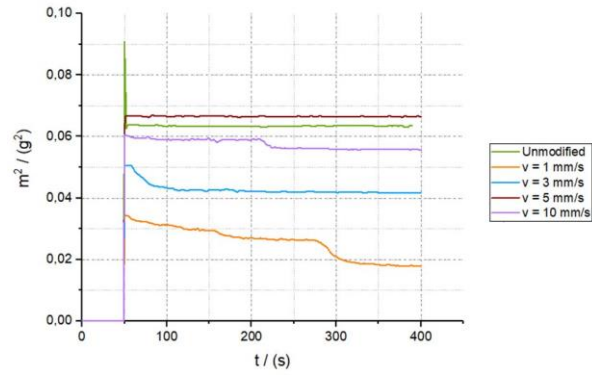


Figure 33 - Time evolution of the gain, in mass, for glycerol.

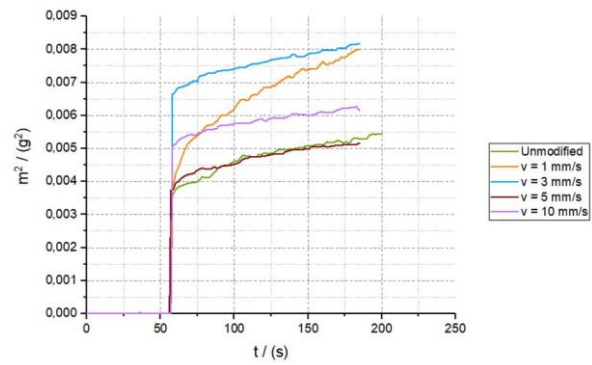


Figure 34 - Time evolution of the gain, in mass, for o-xylene.

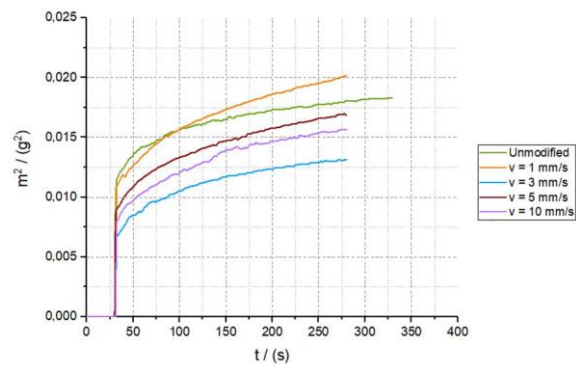


Figure 35 - Time evolution of the gain, in mass, for THF.

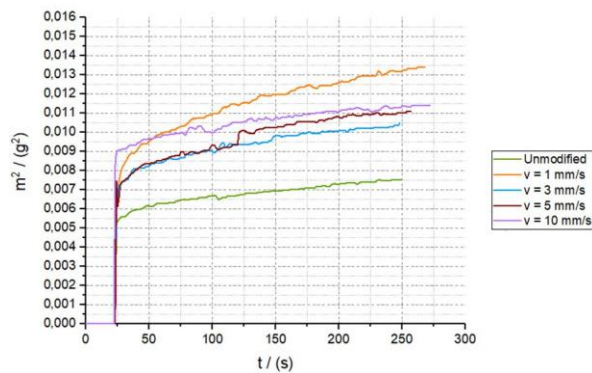
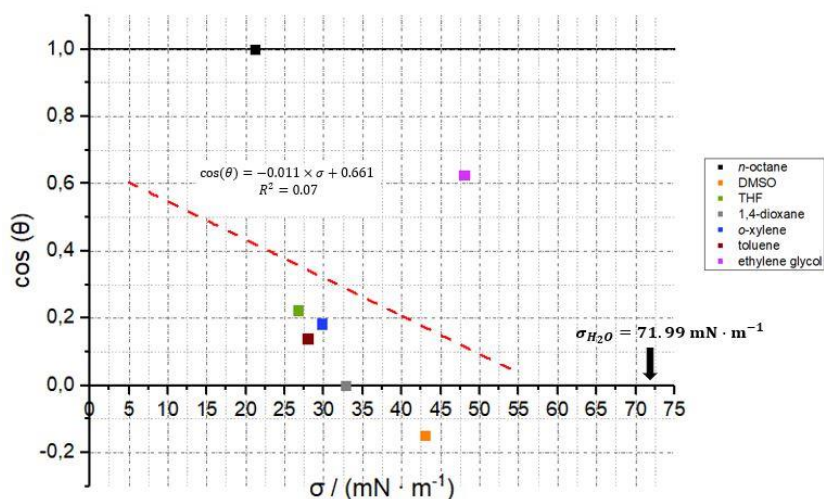
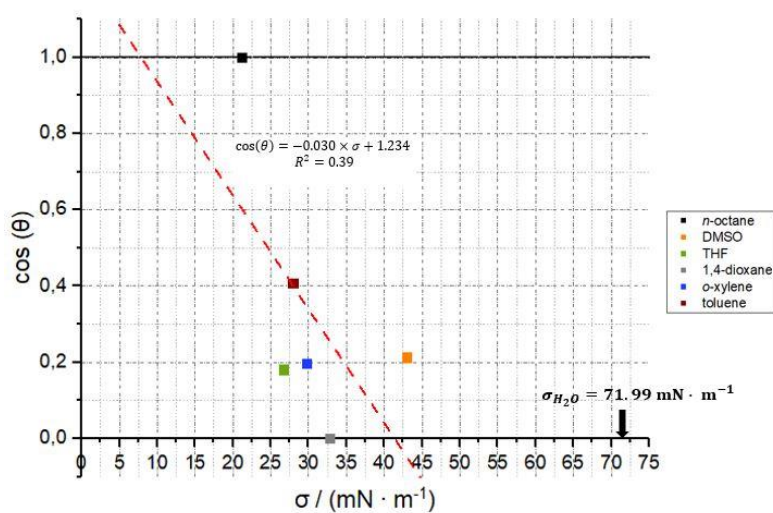
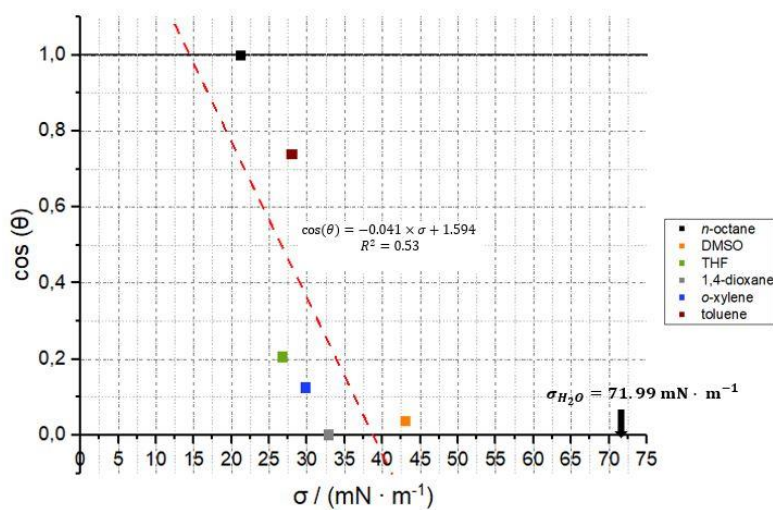


Figure 36 - Time evolution of the gain, in mass, for toluene.


 Figure 37 - Zisman plot for unmodified GDL (*n*-octane as reference solvent).

 Figure 38 - Zisman plot for laser modified GDL $v=3 \text{ mm} \cdot \text{s}^{-1}$ (*n*-octane as reference solvent).

 Figure 39 - Zisman plot for laser modified GDL $v=5 \text{ mm} \cdot \text{s}^{-1}$ (*n*-octane as reference solvent).

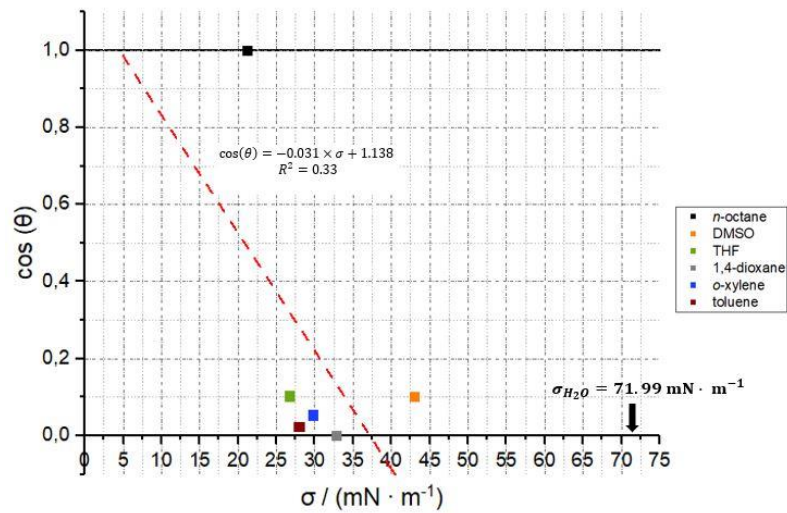


Figure 40 - Zisman plot for laser modified GDL $v=10 \text{ mm} \cdot \text{s}^{-1}$ (n-octane as reference solvent).

- n-hexane as reference solvent (2nd set of experiments)

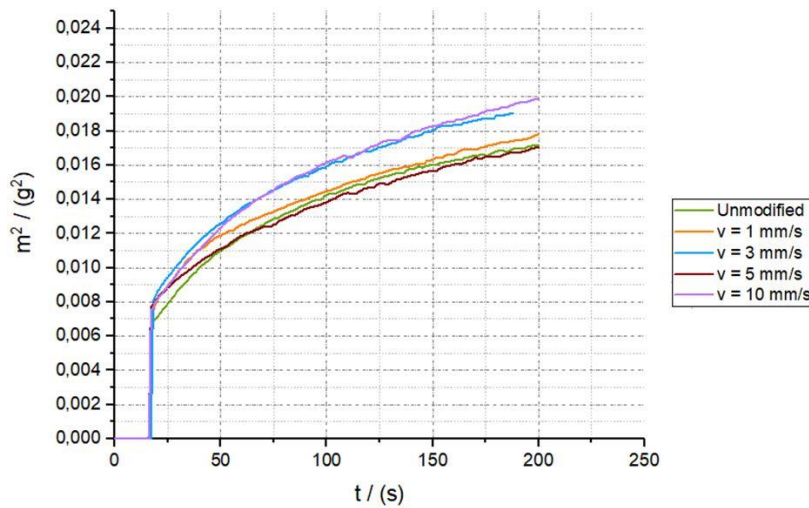


Figure 41 - Time evolution of the gain, in mass, for n-hexane.

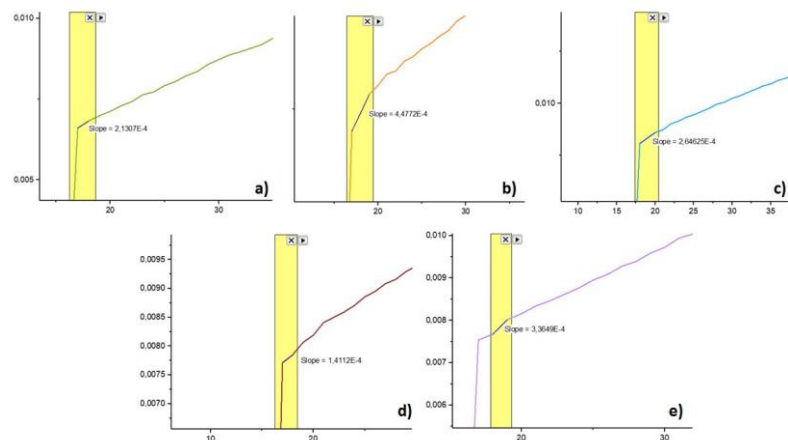


Figure 42 - Determined slopes for unmodified (a) and laser modified GDLs velocities 1 (b), 3 (c), 5 (d) and 10 (e) $\text{mm} \cdot \text{s}^{-1}$ (Origin®) for n-hexane.

Table 29 - Evaluation of the Washburn constants for n-hexane as reference solvent.

Sample	C_w
Unmodified GDL	8.913×10^{-18}
Laser modified GDL $v=1 \text{ mm} \cdot \text{s}^{-1}$	1.873×10^{-17}
Laser modified GDL $v=3 \text{ mm} \cdot \text{s}^{-1}$	1.107×10^{-17}
Laser modified GDL $v=5 \text{ mm} \cdot \text{s}^{-1}$	5.903×10^{-18}
Laser modified GDL $v=10 \text{ mm} \cdot \text{s}^{-1}$	1.408×10^{-17}

Table 30 - Resume of the contact angles, determined for n-hexane as reference solvent.

	Solvent	Unmodified GDL	Laser modified GDL $v=1 \text{ mm} \cdot \text{s}^{-1}$	Laser modified GDL $v=3 \text{ mm} \cdot \text{s}^{-1}$	Laser modified GDL $v=5 \text{ mm} \cdot \text{s}^{-1}$	Laser modified GDL $v=10 \text{ mm} \cdot \text{s}^{-1}$
Contact angle θ (°)	n-hexane	0	0	0	0	0
	DMSO	108.97	93.77	74.79	83.99	81.04
	THF	81.14	75.49	77.06	55.87	80.83
	Ethylene glycol	-	105.54	-	-	-
	1,4-dioxane	89.95	89.95	89.97	89.67	89.86
	o-xylene	66.39	67.77	75.89	69.96	85.21
	Toluene	72.27	53.48	59.80	-	87.94

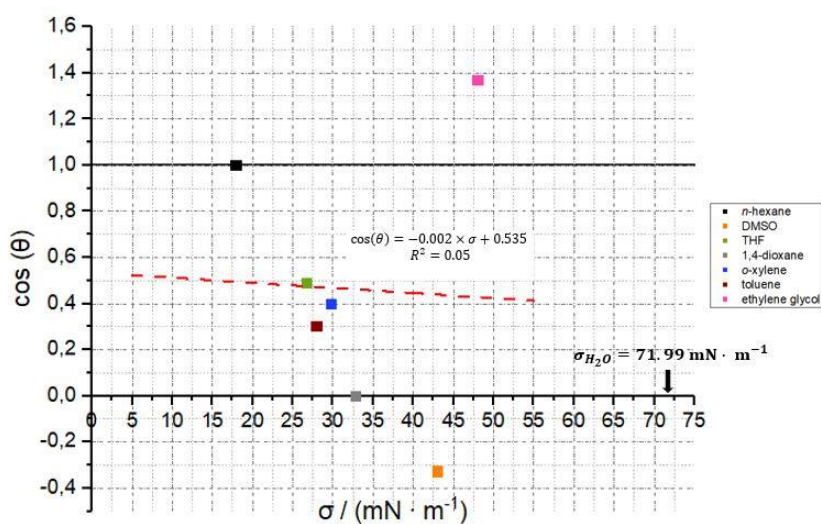


Figure 43 - Zisman plot for unmodified GDL (n-hexane as reference solvent).

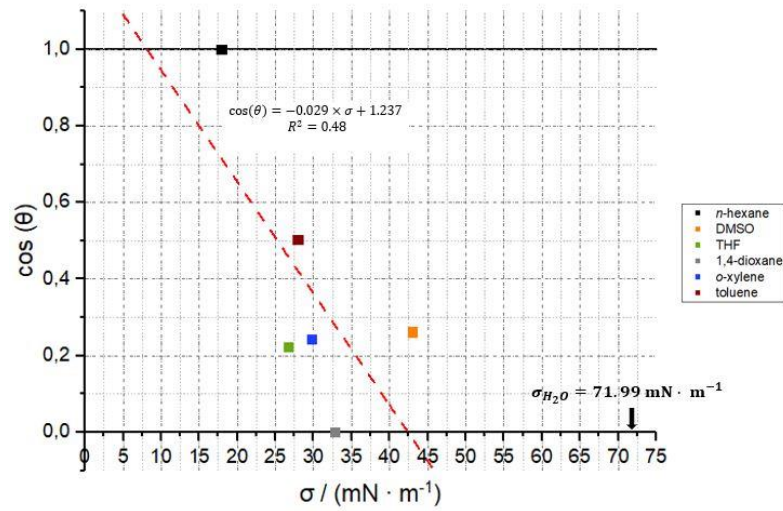


Figure 44 - Zisman plot for laser modified GDL $v=3 \text{ mm} \cdot \text{s}^{-1}$ (n-hexane as reference solvent).

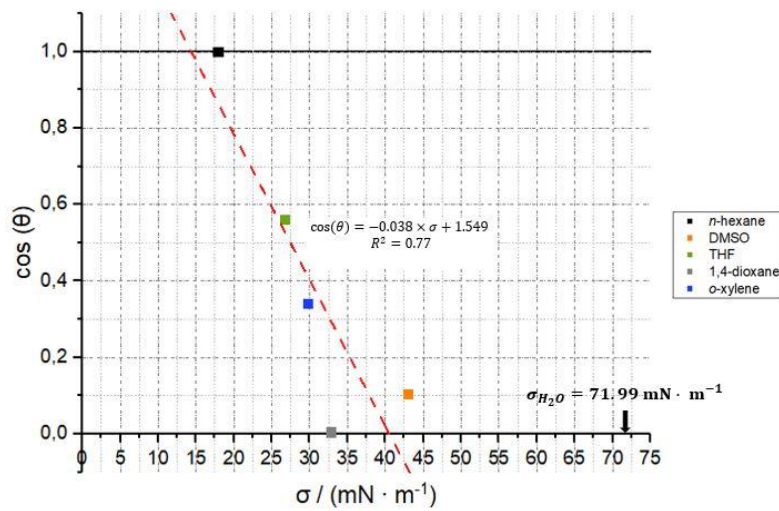


Figure 45 - Zisman plot for laser modified GDL $v=5 \text{ mm} \cdot \text{s}^{-1}$ (n-hexane as reference solvent).

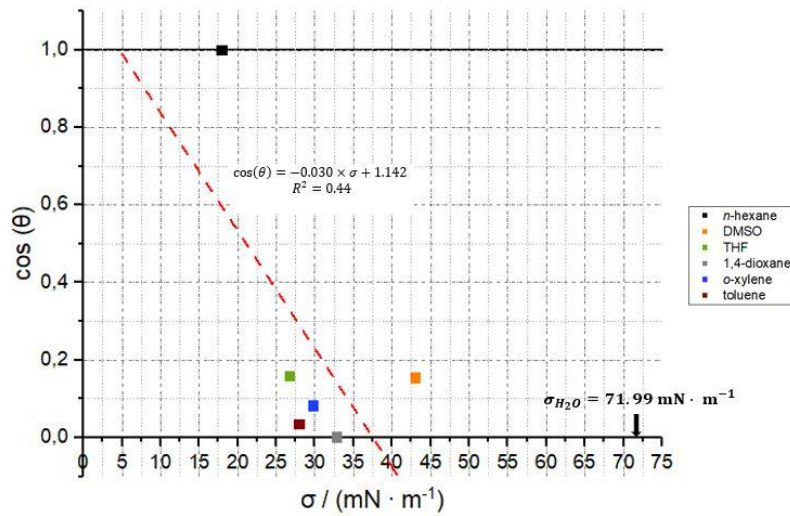


Figure 46 - Zisman plot for laser modified GDL $v=10 \text{ mm} \cdot \text{s}^{-1}$ (n-hexane as reference solvent).

• n-heptane as reference solvent (3rd set of experiments)

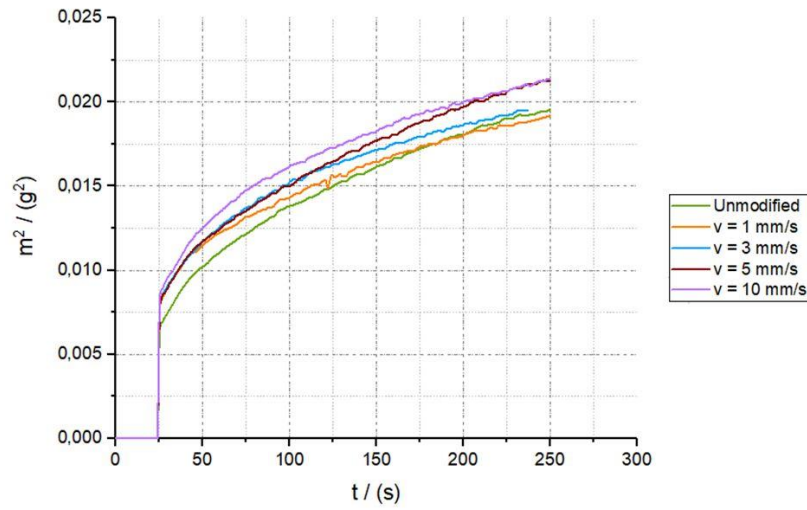


Figure 47 - Time evolution of the gain, in mass, for n-heptane.

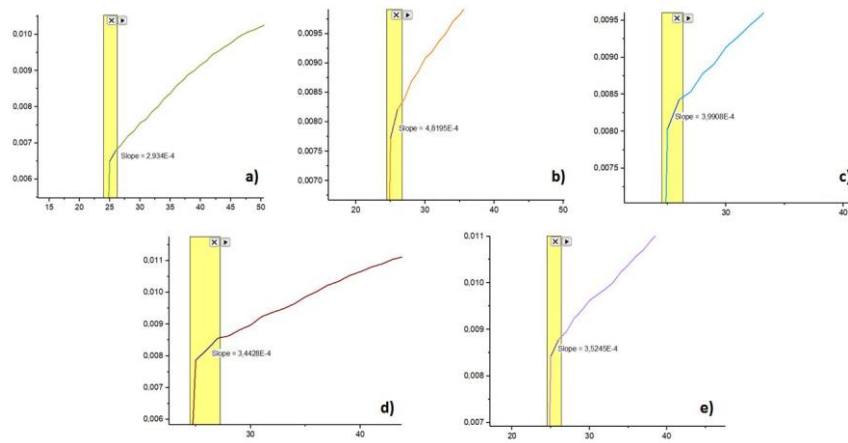


Figure 48 - Determined slopes for unmodified (a) and laser modified GDLs velocities 1 (b), 3 (c), 5 (d) and 10 (e) mm·s⁻¹ (Origin®) for n-heptane.

Table 31 - Evaluation of the Washburn constants for n-heptane as reference solvent.

Sample	C_w
Unmodified GDL	1.214×10^{-17}
Laser modified GDL $v=1 \text{ mm} \cdot \text{s}^{-1}$	1.994×10^{-17}
Laser modified GDL $v=3 \text{ mm} \cdot \text{s}^{-1}$	1.651×10^{-17}
Laser modified GDL $v=5 \text{ mm} \cdot \text{s}^{-1}$	1.425×10^{-17}
Laser modified GDL $v=10 \text{ mm} \cdot \text{s}^{-1}$	1.458×10^{-17}

Table 32 - Resume of the contact angles, determined for n-heptane as reference solvent.

	Solvent	Unmodified GDL	Laser	Laser	Laser	Laser
			modified GDL $v=1 \text{ mm}\cdot\text{s}^{-1}$	modified GDL $v=3 \text{ mm}\cdot\text{s}^{-1}$	modified GDL $v=5 \text{ mm}\cdot\text{s}^{-1}$	modified GDL $v=10 \text{ mm}\cdot\text{s}^{-1}$
Contact angle $\theta \text{ (}^{\circ}\text{)}$	n-heptane	0	0	0	0	0
	DMSO	103.81	93.54	79.87	87.51	81.35
	THF	68.96	76.39	81.36	76.55	81.15
	Ethylene glycol	-	104.57	-	-	-
	1,4-dioxane	89.96	89.96	89.98	89.86	89.86
	o-xylene	72.90	69.19	80.60	81.84	85.37
	Toluene	77.08	56.02	70.29	33.92	88.02

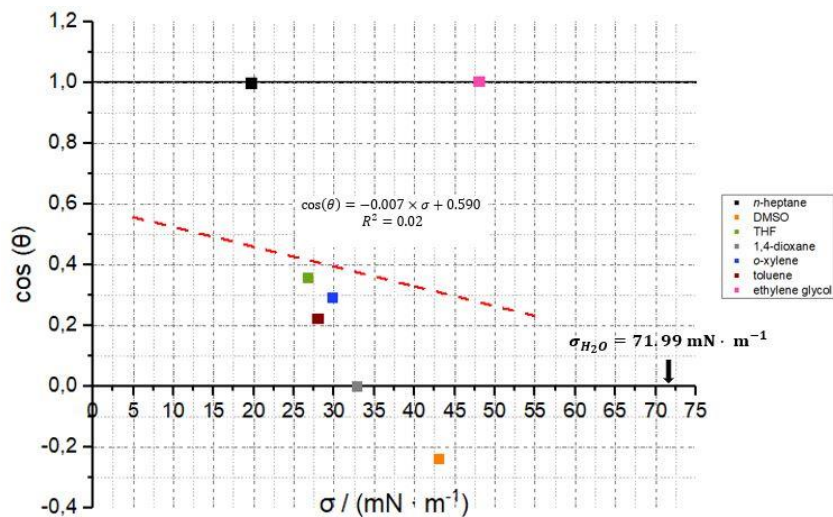
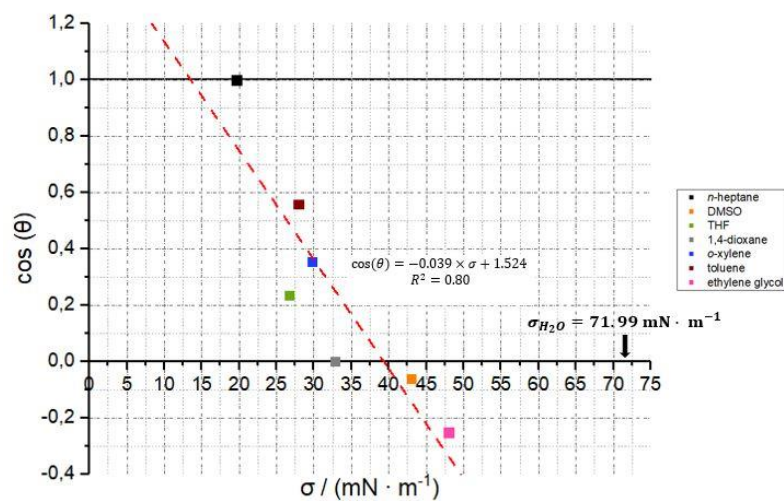


Figure 49 - Zisman plot for unmodified GDL (n-heptane as reference solvent).


 Figure 50 - Zisman plot for laser modified GDL $v=1 \text{ mm} \cdot \text{s}^{-1}$ (n-heptane as reference solvent).

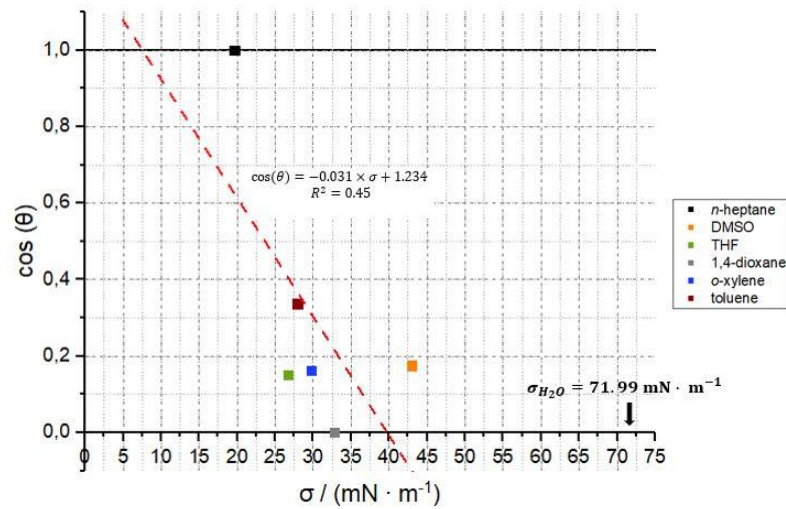


Figure 51 - Zisman plot for laser modified GDL $v=3 \text{ mm} \cdot \text{s}^{-1}$ (n-heptane as reference solvent).

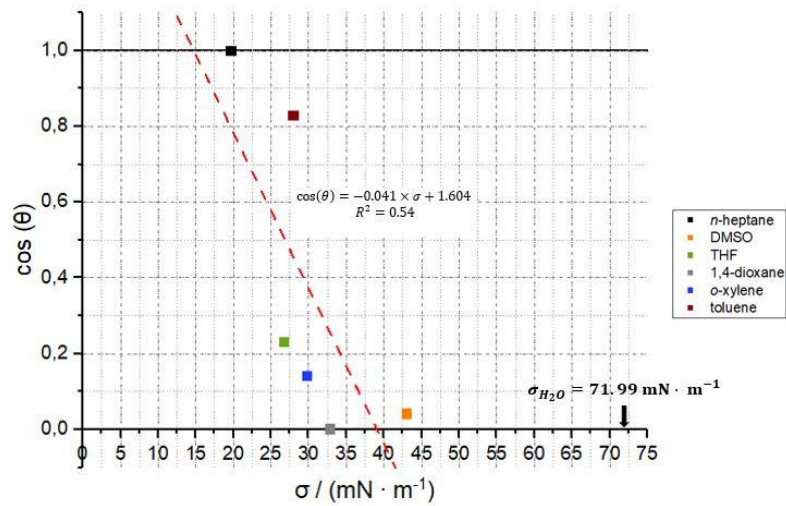


Figure 52 - Zisman plot for laser modified GDL $v=5 \text{ mm} \cdot \text{s}^{-1}$ (n-heptane as reference solvent).

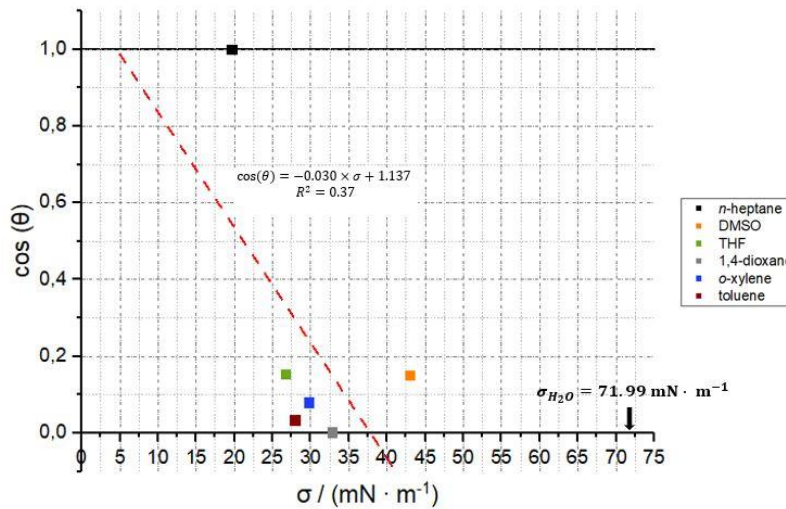


Figure 53 - Zisman plot for laser modified GDL $v=10 \text{ mm} \cdot \text{s}^{-1}$ (n-heptane as reference solvent).

Results and discussion regarding the Owens-Wendt model

- n-decane as reference solvent (4th set of experiments)

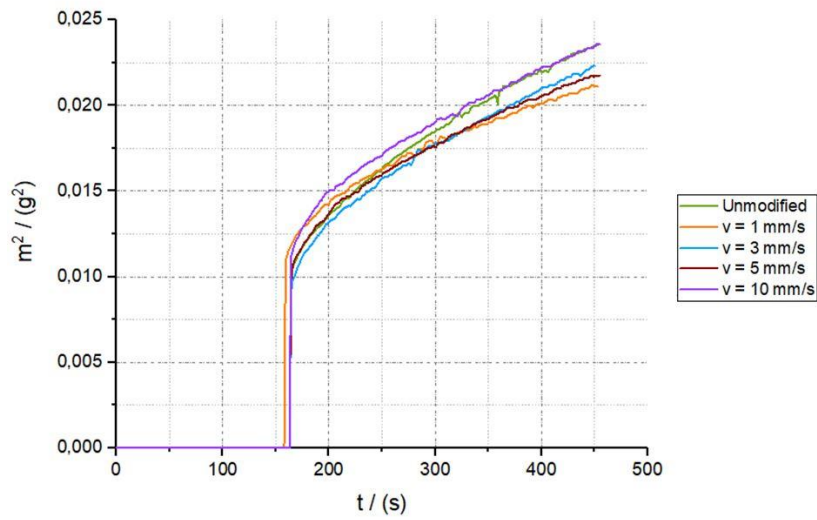


Figure 54 - Time evolution of the gain, in mass, for n-decane.

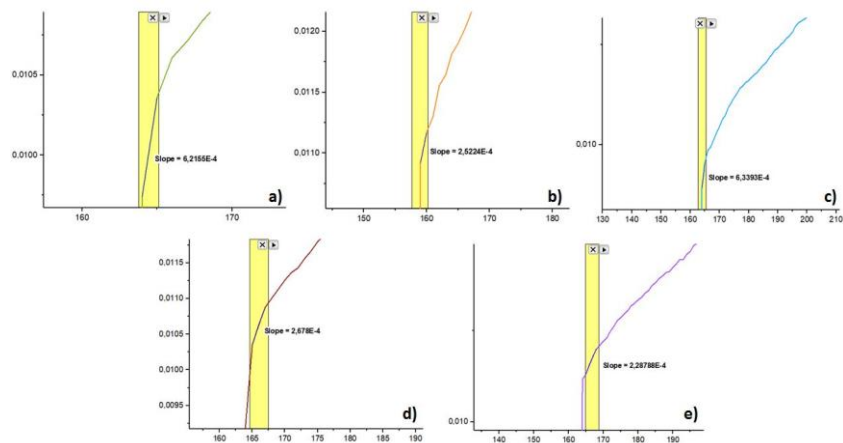


Figure 55 - Determined slopes for unmodified (a) and laser modified GDLs velocities 1 (b), 3 (c), 5 (d) and 10 (e) $\text{mm}\cdot\text{s}^{-1}$ (Origin®) for n-decane.

Table 33 - Evaluation of the Washburn constants for n-decane as reference solvent.

Sample	C_w
Unmodified GDL	4.107×10^{-17}
Laser modified GDL $v=1 \text{ mm}\cdot\text{s}^{-1}$	1.667×10^{-17}
Laser modified GDL $v=3 \text{ mm}\cdot\text{s}^{-1}$	4.189×10^{-17}
Laser modified GDL $v=5 \text{ mm}\cdot\text{s}^{-1}$	1.769×10^{-17}
Laser modified GDL $v=10 \text{ mm}\cdot\text{s}^{-1}$	1.512×10^{-17}

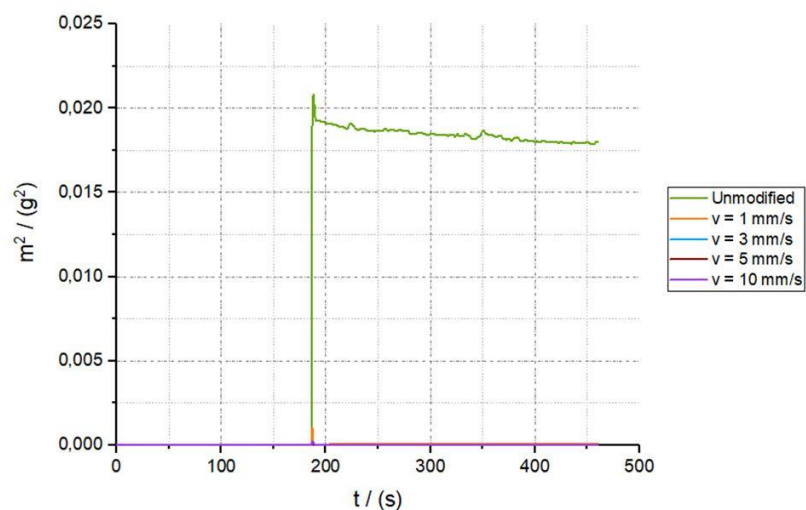


Figure 56 - Time evolution of the gain, in mass, for benzyl alcohol.

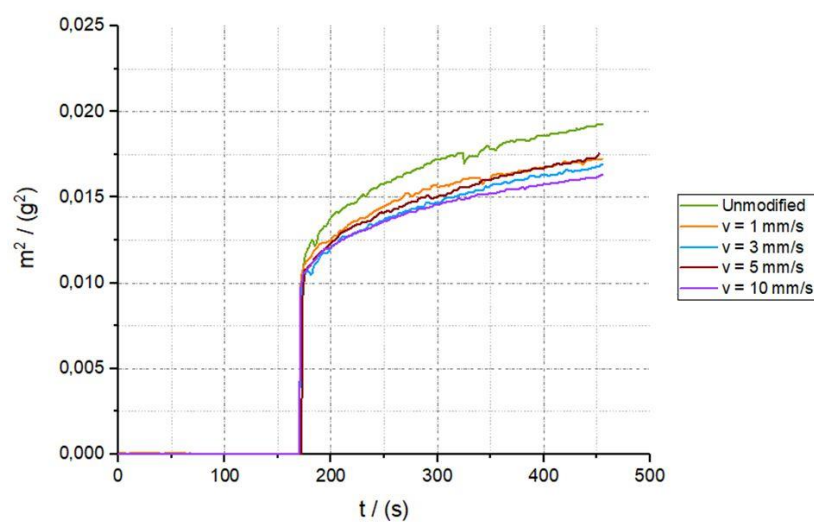


Figure 57 - Time evolution of the gain, in mass, for cyclohexane.

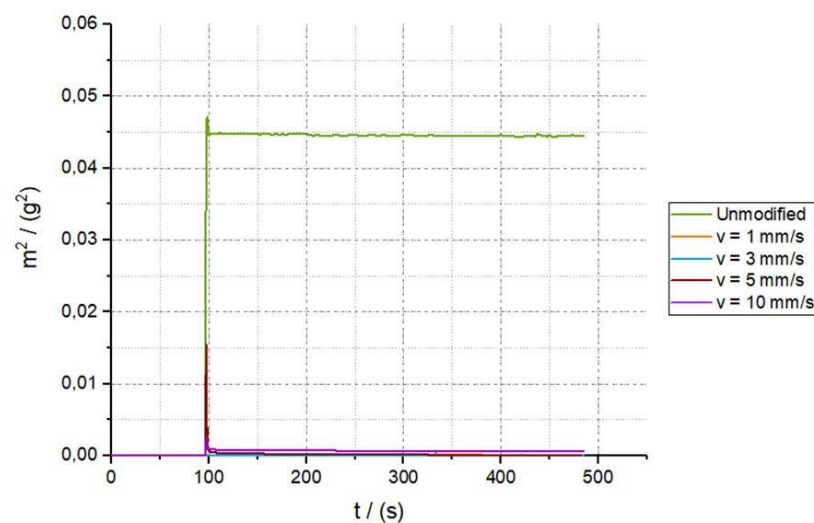


Figure 58 - Time evolution of the gain, in mass, for diiodomethane.

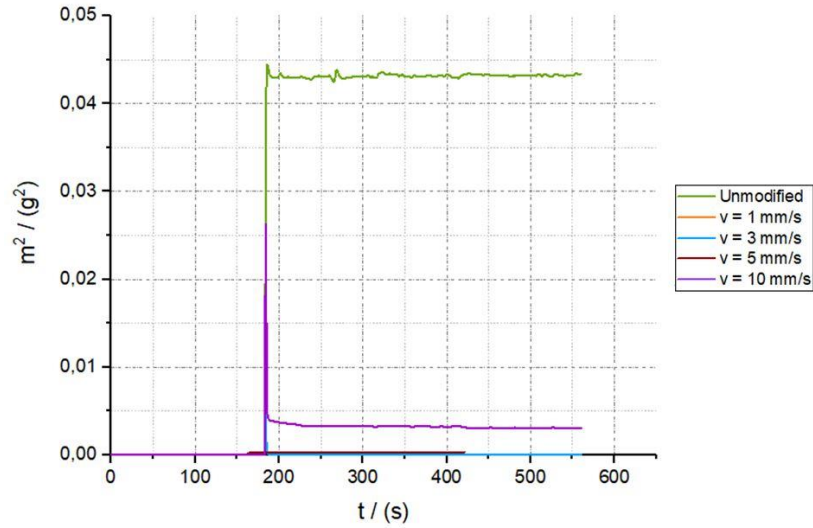


Figure 59 - Time evolution of the gain, in mass, for ethylene glycol.

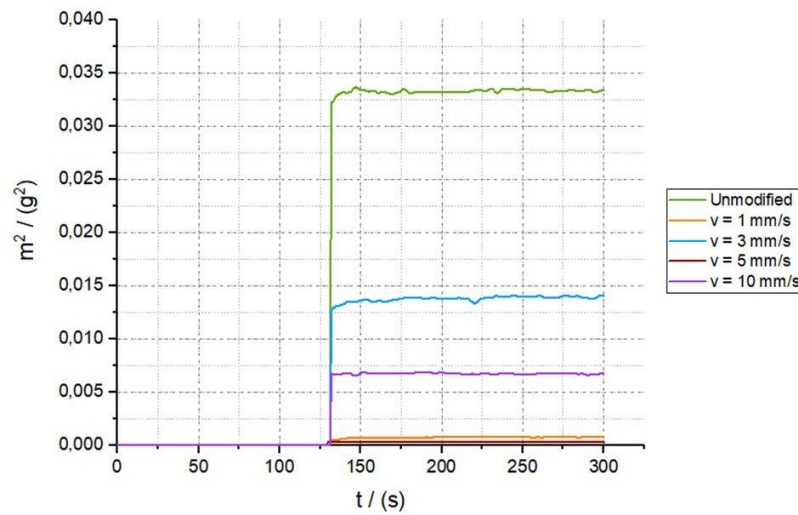


Figure 60 - Time evolution of the gain, in mass, for formamide.

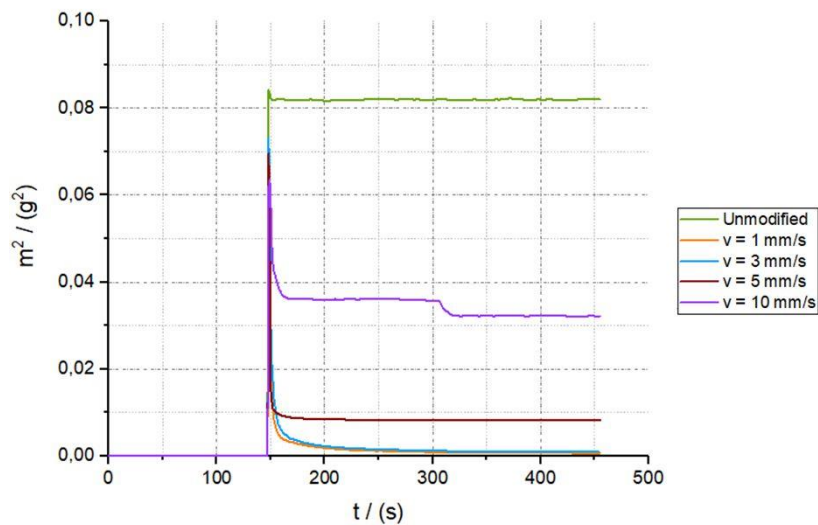


Figure 61 - Time evolution of the gain, in mass, for glycerol.

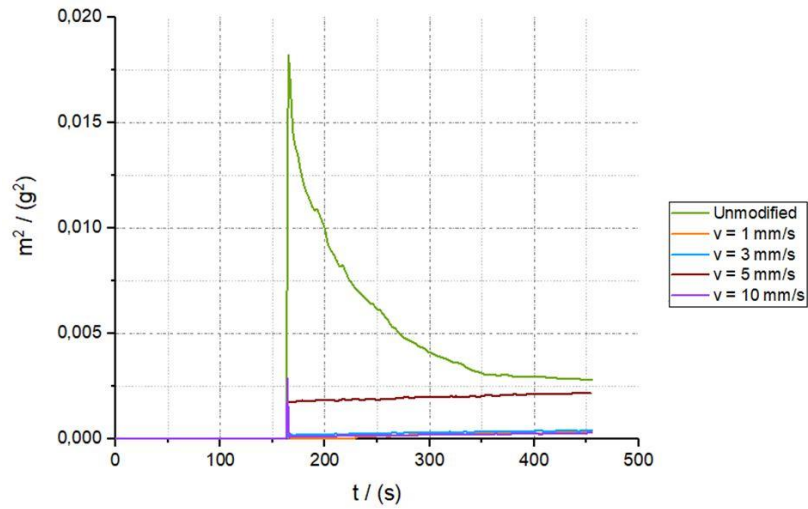


Figure 62 - Time evolution of the gain, in mass, for methyl benzoate.

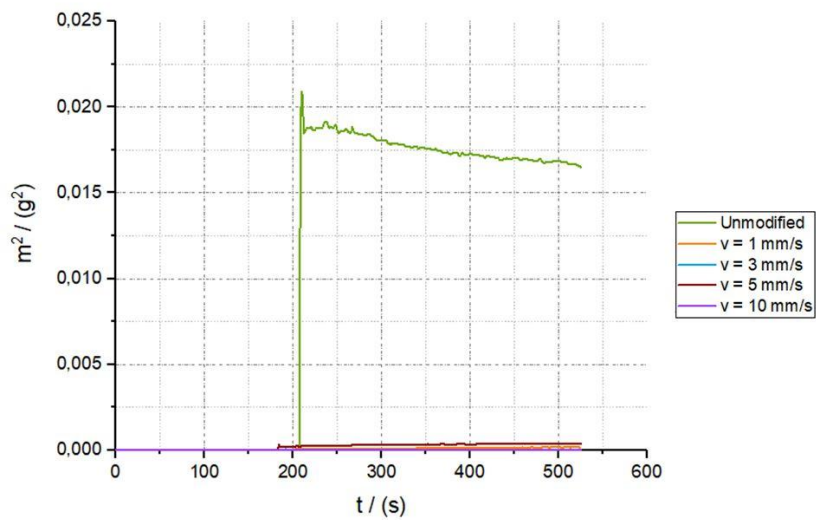


Figure 63 - Time evolution of the gain, in mass, for nitromethane.

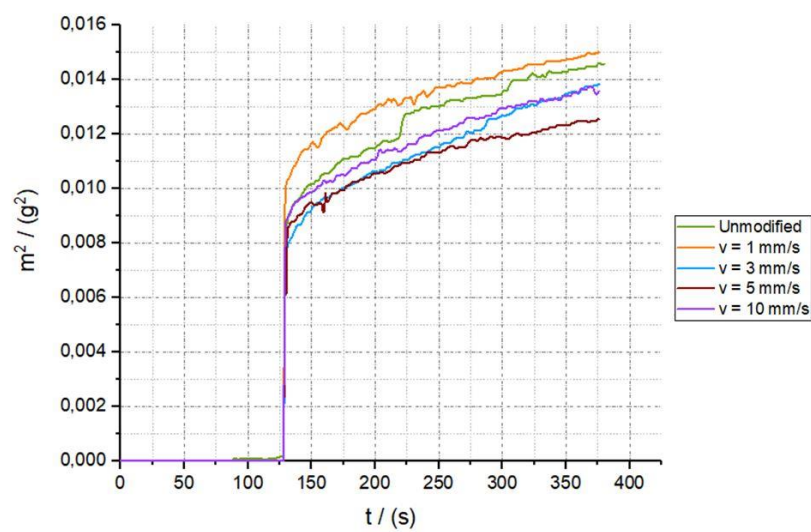


Figure 64 - Time evolution of the gain, in mass, for n-tetradecane.

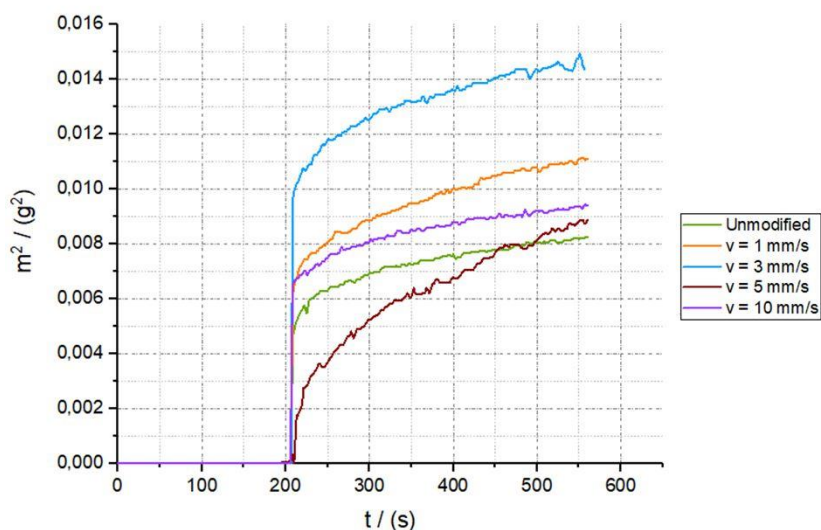


Figure 65 - Time evolution of the gain, in mass, for toluene.

Table 34 - Resume of the contact angles, determined for n-decane as reference solvent.

	Solvent	Unmodified GDL	Laser	Laser	Laser	Laser
			modified GDL $v=1 \text{ mm}\cdot\text{s}^{-1}$	modified GDL $v=3 \text{ mm}\cdot\text{s}^{-1}$	modified GDL $v=5 \text{ mm}\cdot\text{s}^{-1}$	modified GDL $v=10 \text{ mm}\cdot\text{s}^{-1}$
Contact angle $\theta (^{\circ})$	n-decane	0	0	0	0	0
	cyclohexane	52.35	38.04	50	71.35	30.03
	n-tetradecane	57.01	47.24	65.57	73.14	46.33
	Toluene	84.57	42.28	82.47	83.32	81.79
	Nitromethane	97.33	89.95	90.07	90.61	91.47
	Methyl benzoate	131.70	89.36	109.39	86.23	79.87
	Benzyl alcohol	94.98	104.88	104.84	124.43	128.43
	Ethylene glycol	106.80	108.99	150.71	96.42	135.89
	Diiodomethane	101.50	97.20	93.27	94.27	116.91
	Formamide	71.95	85.77	80.31	88.02	84.53

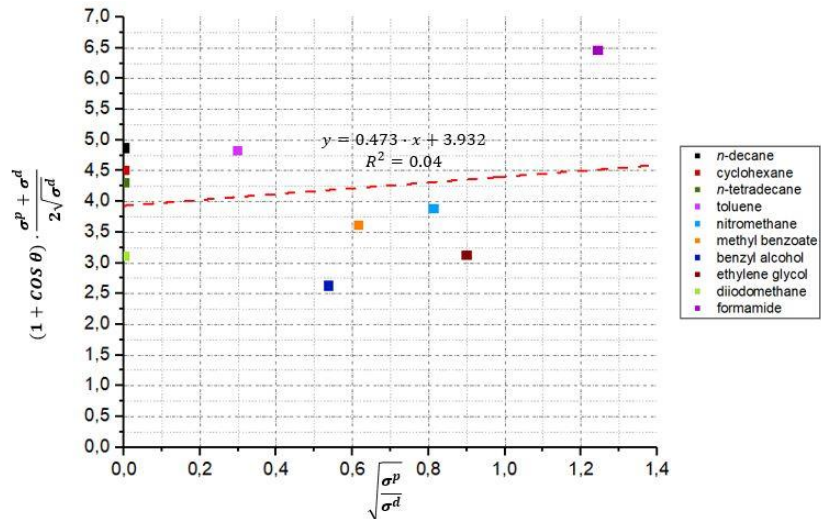


Figure 66 - Owens-Wendt two-parameter model for laser modified GDL $v=1 \text{ mm} \cdot \text{s}^{-1}$ (n-decane as reference solvent).

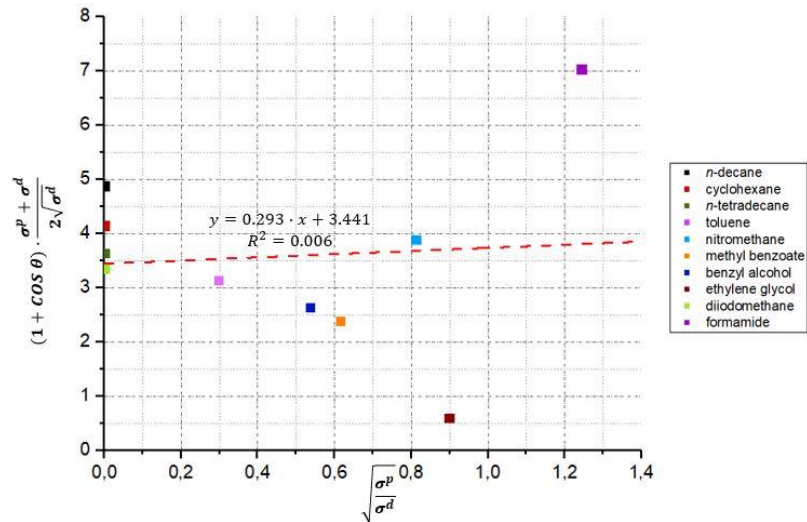


Figure 67 - Owens-Wendt two-parameter model for laser modified GDL $v=3 \text{ mm} \cdot \text{s}^{-1}$ (n-decane as reference solvent).

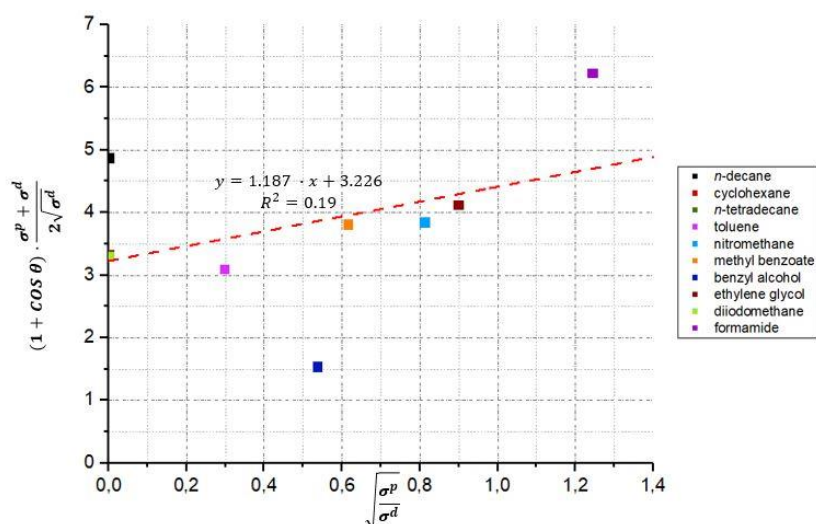


Figure 68 - Owens-Wendt two-parameter model for laser modified GDL $v = 5 \text{ mm} \cdot \text{s}^{-1}$ (n-decane as reference solvent).

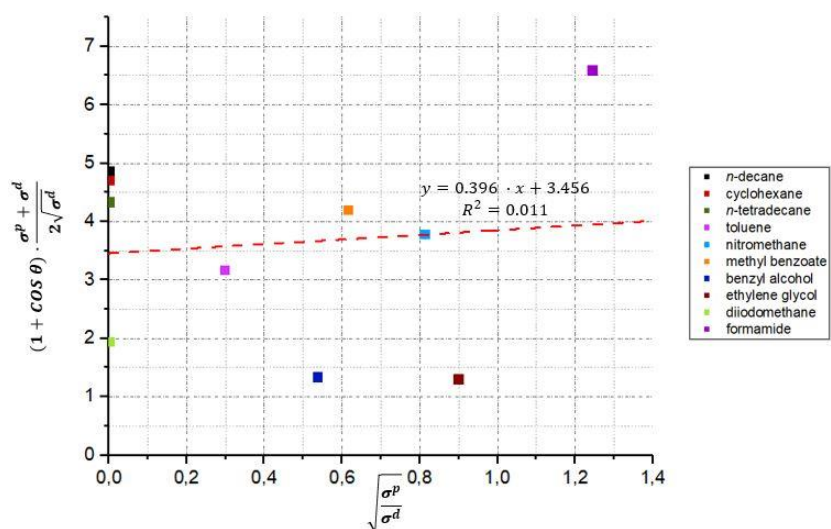


Figure 69 - Owens-Wendt two-parameter model for laser modified GDL $v = 10 \text{ mm} \cdot \text{s}^{-1}$ (n-decane as reference solvent).