Doctoral Thesis

Novel Gas Diffusion Layers with Patterned Wettability for Advanced Water Management Strategies in Polymer Electrolyte Fuel Cells

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Novel Gas Diffusion Layers with Patterned Wettability for Advanced Water Management Strategies in Polymer Electrolyte Fuel Cells

A thesis submitted to attain the degree of
DOCTOR OF SCIENCES of ETH ZURICH
(Dr. sc. ETH Zurich)

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Summary

Research in academia and industry strives to develop more efficient and clean energy technologies to power stationary and mobile applications. Pursuant to this goal, extensive developments have been made in the field of polymer electrolyte fuel cells (PEFCs) over the last 20 years. PEFCs are one of the most promising candidates for automobile applications due to their high efficiency, power density and lack of pollutants. As a result, the first fuel cell cars are available on the market; however, still at elevated price. To facilitate the vast market integration of PEFC vehicles, the efficiency needs to be further improved, especially under high current densities. In other words, for a given power output cost would be reduced if performance is maximized. In this context, this dissertation work aims to improve power density of PEFCs through an advanced water management. While some water is needed to humidify membrane and ionomer in catalysts layers, excessive amounts of water in the porous layers lead to increased mass transport resistances for the gases, reducing thereby the performance. By using the materials developed within this work, water leaves the cell throughout pre-designed hydrophilic regions, while gases travel preferentially through the remaining hydrophobic, dry, low-resistance pathways.

A novel type of gas diffusion layer (GDL), consisting on an arrangement of hydrophilic and hydrophobic domains, has been developed within this PhD work. This thesis starts by describing the concept of GDLs with patterned wettability and the synthetic method which is based on electron radiation grafting of the polymeric coating. This first part contains an introduction and a collection of experimental methods and techniques. At the end of this part, a proof-of-concept showing the promising potential of these materials is provided.

Later, a thorough systematic study focuses on finding experimental conditions to synthesize hydrophilic surfaces by free radical polymerization reactions. Once successful conditions were found, they were applied to locally irradiated materials by using blocking masks. A combination of experiments and numerical simulations is presented aiming the production of high quality patterns. Then, the modified materials were characterized based on their capillary pressure characteristic. From this study, it was learnt that microstructure and coating load are the material parameters affecting water
segregation the most. Finally, the best candidates were tested *operando* in fuel cells under various conditions (temperatures, gas humidities and assemblies). Positively, it was found that the use of GDLs with patterned wettability improve PEFC performance due to a reduction in mass transport losses. The simultaneously obtained neutron radiographs proved that the new water distribution, according to the engineered hydrophilic patterns, justifies the improvements in power density.
**Zusammenfassung**


Danach legt eine genaue systematische Untersuchung dar, wie Versuchsbedingungen gefunden werden, um hydrophile Oberflächen mit freier radikalischer Polymerisation zu synthetisieren und wie dieses Wissen für die Herstellung poröser Substrate transferiert.
Acknowledgments

The present doctoral work has been carried out at the Electrochemistry Laboratory of the Paul Scherrer Institut between April 2013 and November 2016. Back in 2013, carrying out a PhD study in Switzerland was not an easy decision to be made. More than three years later, I feel that I could not have taken a better choice. And let’s be honest, I would have never gotten here without the help and support of different colleagues and friends, to whom the following paragraphs are dedicated.

First, I would like to thank Pierre, Thomas, Lorenz and Prof. Wokaun for giving me the opportunity of working on such a fascinating project. I want to thank my Doktorvater, Prof. Thomas J. Schmidt, for his great supervision, flexibility, sense of humor, accessibility and always excellent professional and personal advice, helping me a lot to develop as scientist. I want to thank my co-supervisor, Dr. Lorenz Gubler, for his scientific support, exemplary availability, fun moments and his accurate English language corrections. Prof. Wokaun is greatly acknowledged for co-examining this thesis despite of a very busy professional agenda.

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The students whom I supervised are deeply acknowledged. Patricia Gröninger, Harlin Brandvold and Victoria Manzi have made notable contributions to this PhD work and made me learn many things which I will carry along for the coming years. It makes me tremendously happy that Victoria has taken over the work of modified gas diffusion layers, meaning that a member of the Playa Team will be taking good care of the second generation of these materials. I wish you the best for the rest of the journey.

To the current and former members of my group I feel grateful: Muriel, Johannes, Magali, Dirk, etc. Thanks to your personalities and technical skills there was always a dynamic and friendly atmosphere. In particular, I feel indebted to Dr. Johannes Biesdorf for three amazing years of working together. Your motivation, always positive attitude and support during never-ending neutron nights have been of great help for me. For the
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Additionally, I want to thank the members of the Membrane group (Véro, Joanna, Albert, Lukas), the Catalysis group (Susan, Annett, Sandra, Alex, Tobi, Emi) and the “X-ray guys” (Adrien, Felix, Jens, Basti) for a great collaboration and discussions. Dr. Mario El Kazzi and Dr. Daniel Streich are also acknowledged for their help and discussions and Cordelia and Ursula for administrative matters. The NIAGs also provided important support (Peter, Jan). Prof. Magnus Kristiansen is acknowledged for the use of electron beam and Dr. Celestino Padeste for providing access to their laboratories. Dr. Yohann Thomas (CEA) and Dr. Yeh-Hung Lai (General Motors) are also acknowledged for their technical help.

In order for me to function properly, I always needed to balance work, sport and personal life. In this context, my Hönggi friends extensively exceeded the expectations. I will not forget the day when, by absolute chance, I met Boos at ASVZ which finally lead to my signing at SV Höngg. Believe me when I say that my life here in Switzerland suddenly became far more interesting - as commonly said “the people make the place”. To current and former players I owe the fun times, the fast integration into the culture and the possibility of still enjoying football at a fairly good level. Some of you even open the doors of your homes for me! Especially to Tom, Rafi, Laurent, Boos, Simon, Paul, Marc, Micke, Forny, Claude, Philipp and many others, I will always be thankful to you for having treated me like you did during this time. Many thanks go to Ainara, Diego and Juli for their continuous support and care outside the office.

Finally, let me address my family, to whom this work is dedicated:

Para Blanca, Guillermo y mis padres – os pido perdón por estos años de ausencias y por ser un culo inquieto. Y os agradezco todo lo que me habéis dado durante estos años, pues no habría llegado hasta aquí sin teneros en mi vida. A Guille por superarse y reinventarse cada día. A mi padre, por inculcarme principios como la disciplina, el trabajo duro y la humildad. A mamá, por tu perfeccionismo y por comerte el filete con más nervios. Y a Blanca, por tu bondad y amor, por apoyar mis locuras y, sobretodo, por ser mi compañera en la aventura.
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Declaration of self-citations

This PhD thesis is a cumulative doctoral thesis that contains 4 peer-reviewed published manuscripts, one submitted manuscript and one published annual report. Additionally, some new parts have been written (Chapter 1, 2 and 8). Chapters 3, 4, 5, 6 and 7 are composed of an executive summary followed by the reproduced publication. The publications accumulated in this thesis are enumerated in the following table:

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The individual contributions of all co-authors are given here:

- **A. Forner-Cuenca** performed and designed experiments, analyzed and illustrated data and wrote the manuscripts.
- **J. Biesdorf** assisted performing experiments and discussed results (P1, P4-P6).
- **V. Manzi-Orezzoli** assisted and performed the experiments and discussed results (P2-P5).
- **P. Boillat** assisted in experiment design, discussed results, supervised the work, evaluated and edited manuscripts.
- **L. Gubler** and **T.J. Schmidt** discussed results, supervised the work, evaluated and edited manuscripts.
- **P. M. Kristiansen** assisted performing electron beam irradiation and discussed results (P1 and P2).
- **A. Lamibrac** and **F.N. Büchi** assisted performing the X-ray tomography experiments and discussed results (P4).
- **P. Gröninger** assisted in and performed imbibition dynamics experiments and discussed results (P6).
- **D. Streich** assisted performing the infrared spectroscopy measurements, and discussed results (P3).
- **M. El Kazzi** assisted in and performed the X-ray photoelectron spectroscopy measurements and discussed results (P3).

Finally, the following table contains the origin of manuscripts’ excerpts used in the different chapters:

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Chapter 1. Introduction

This first chapter includes a brief introduction to fuel cells, with the focus on Polymer Electrolyte Fuel Cells (PEFCs). After a description of the typical cell assembly and its components, the main thermodynamic relationships and performance loss indicators will be described. Later, further details related to mass transport losses will be discussed in the light of diffusivity, permeability and capillary transport in porous materials, specifically gas diffusion layers. Once these fundamental concepts have been introduced, the gas diffusion layer production costs are evaluated. The chapter closes by introducing the idea of gas diffusion layers with patterned wettability, both in terms of the proposed synthetic method and comparing with previously reported technologies.
1.1 Motivation

1.1.1 The need for clean power technologies

The transition to a fossil fuels-free based energy economy is one of the greatest challenges faced by humankind\(^1\). There are many scientific evidences linking the starting of the industrial age and population growth with the increase of atmospheric CO\(_2\) concentration\(^2\) and consequent average temperature and sea level rise\(^3\). According to the International Energy Agency, the total primary energy consumption worldwide, measured in tonnes of oil equivalent (toe), was 9.43 billion (10\(^9\)) toe in 2014 and is expected to be 12.2 or 10.6 (depending on the scenario) by 2045. Worldwide CO\(_2\) emissions accounted for 32.4 Bt/year in 2014 and continue to increase at a similar rate\(^4\). On top of that, fossil fuels, which took millennia to accumulate, are rapidly being depleted. It therefore stands to reason that we need to develop new energy sources which are affordable, accessible and sustainable.

The concept of “the hydrogen economy” promises to fulfil all these requirements (Figure 1.1). Hydrogen should be used as energy carrier, storing large amounts of chemical energy, and can be used whenever needed in both stationary and mobile applications (transportation)\(^5-7\).

![Figure 1.1 - Schematics featuring a hydrogen economy based cycle.](image-url)
Nowadays industrial hydrogen production is mainly based on methane steam reforming and consequently contributes to greenhouse gas emissions\(^8\). However, alternative technologies, e.g., water electrolysis, are being developed at the moment\(^8, 9\). If the energy input needed to produce the hydrogen comes from renewable sources, then there are virtually zero emissions in the whole energy conversion cycle. Central to the concept and the success of hydrogen technologies are fuel cells. Fuel cells are reactors which transform chemical energy directly into electrical energy via an electrochemical conversion.

### 1.1.2 Reducing the cost of fuel cells

The first generation of fuel cell vehicles has been launched to the market (Toyota Mirai, Hyundai ix35). Regarding automotive applications, Polymer Electrolyte Fuel Cells (PEFCs) are arguably the most promising system. The United States Department of Energy (DOE) has set strict cost targets for fuel cell technologies that will permit their widespread integration into the market\(^10\). As can be seen in Figure 1.2 the estimates of PEFC system cost were substantially lowered in the period between 2006 and 2010. While further cost cut-downs have continued in the following years, they are comparatively less significant. The estimated system cost in 2015 was \(~$53/kW\) if a high-volume of manufacturing (500 000 units/year) is considered. The DOE targets a system cost of $40/kW for 2020 and an ultimate cost target of $30/kW, again at large-scale production.

![Figure 1.2 - Estimated automotive fuel cell system costs over the past years and future targets, assuming a production rate of 500 000 units/year. Adapted from Ref\(^{10}\).](image)

---

\(^{10}\) Ref to source.
It is, however, obvious that these values are still far away from the commercial reality of PEFCs in terms of production volumes and therefore more realistic values must be provided. According to the DOE, the expected cost of automotive PEFCs based on current technologies is of \( \sim \$280/kW \) for about 20 000 units produced per year. This dissertation work aims to develop advanced porous materials to improve power density of PEFCs. Further improvements in power density will facilitate commercialization. Put another way, for a given power output, PEFCs will require less total area and therefore cost will be reduced.

1.2 Fuel cell fundamentals

Generally speaking, a fuel cell is an energy conversion device that uses chemical energy from a fuel to produce electrical energy. They differentiate themselves from internal combustion engines in that no mechanical conversion step is required and they are different from conventional batteries in that they are continuously fed by reactants allowing them to function unlimitedly – subject to the capacity of the fuel storage. In some detail, the device is composed by two half-cell compartments which are divided by a separator. This separator must conduct ions but impede electron transport and permeation of reactants between the two compartments. Electrochemical reactions occur in each of the half-cells and electrons produced are transported through an external circuit generating the useful electrical power. Several types of fuel cells have been invented and investigated, such as polymer electrolyte fuel cells, direct methanol fuel cells, phosphoric acid fuel cells, solid oxide fuel cells and molten carbonate fuel cells, among others. They notably differ from each other according to the working temperature range, the type of fuel and the ionic transport mechanism. In this work, we focus on PEFCs, which are the most promising devices for automobile applications due to their high power density, realization potential and cost.

1.2.1 Polymer Electrolyte Fuel Cells

PEFCs use hydrogen as fuel and oxygen as oxidant. Most practically used PEFCs are fed with air instead of pure oxygen. While the use of pure oxygen leads to significant improvements of performance\[11, 12\], the major drawback lies in the logistics of production and distribution. PEFCs are composed by a stack of individual units. The individual cells are composed of an arrangement of layers of different materials (details in 1.2.2) providing various functionalities (Figure 1.3). Each of these cells produces a certain voltage and many of them are stacked together in series to generate the desired power output.
Figure 1.3 - Illustration showing main PEFC cell components, the flow direction of gases, charge transport and electrochemical reactions, focusing on the membrane electrode assembly (MEA). The sketch is not to scale.

1.2.2 Cell configuration and components

Structurally speaking, anode and cathode of state-of-the-art PEFCs are constructed symmetrically – although the characteristics of the corresponding layers might be different between anode and cathode. In other words, the different layers are mirrored with respect to the central component, the membrane. In the following paragraphs, each individual layer is described:

- Proton conducting membrane:

The membrane is made of a solid polymer electrolyte and needs to effectively conduct protons ($\sigma \sim 0.1$ S·cm$^{-1}$) and block the transport of electrons and gases. Nafion membranes (DuPont®) are the most widely used materials and are based on perfluorosulfonic acid (PFSA) ionomer, which consists of a sulfonated polytetrafluoroethylene (PTFE, Teflon) backbone and thicknesses in the order of 15-30 μm. The sulfonic acidic groups ($\text{SO}_3^- + \text{H}_3\text{O}^+$) are the anchor point for proton conduction when the membrane is hydrated. Nafion membranes still contribute a significant fraction to the fuel cell costs and therefore research is focused on development of new low-cost types of membranes based on different technologies, such as radiation grafting$^{[13]}$ and hydrocarbon-based membranes$^{[14]}$. 
- **Catalyst layer (CL):**

CLs are porous layers composed of: catalyst particles (typically platinum), a conductive support (carbon) and ionomer (normally PFSA, as in the membrane). They can be either coated on the membrane – in which case the membrane is called a catalyst coated membrane (CCM) – or on the GDL (or MPL) surface. The CLs are typically 5-10 µm thick and coated on both sides of the membrane (or on the inner side of the microporous layers). Generally the catalyst loading (i.e. mass of precious metal per geometric surface area) is higher in the cathodic CL than in the anodic one. This is to increase the available specific surface area to compensate for sluggish oxygen reduction reaction kinetics. It is worth mentioning the importance of the so-called three-phase boundary in the CL. In order for the reactions to take place, there needs to be an interface between solid (particle), liquid (hydronium ions in the hydrated polymer) and gas (oxygen/hydrogen).

- **Microporous layer (MPL):**

The MPLs are one of the latest incorporation to PEFCs. In the last years, they have been intensively investigated and implemented widely. Nowadays, it is accepted that MPLs are a key component to reach high power densities, in particular for conditions with high humidity[15]. MPLs are generally composed of carbon particles (spherical carbon onions or carbon blacks) mixed with a hydrophobic polymer (typically PTFE). Compared to GDLs, they have much smaller porosity (~0.25)[16] and a finer average pore size (~50-200 nm)[17]. Many different MPL production processes have been reported and resulted in layers with broadly distinct properties, such as different hydrophobicity, presence or absence of cracks, and different thicknesses. The specific influences of each material property have not yet been elucidated. However, it seems clear that three main functionalities are provided by the MPLs: (I) their use significantly reduces CL flooding by providing an improved water management, specifically when using fully humidified gases; (II) the electrical contact resistance between CL-MPL is reduced compared of that of CL-GDL due to a more intimate contact and decrease in roughness; (III) membrane and CL degradation seem to be drastically decreased since the MPL has a smoother surface[16, 18].

- **Gas diffusion layer (GDL):**

Since the GDLs represent the centerpiece of this dissertation, we will dedicate a complete section to them (Section 1.5). In short, the GDL thickness is in the range of 100-500 µm, has an approximate porosity of 0.7-0.9 and an average pore diameter of 10-40 µm. The GDL, stacked between membrane (or MPL if they are used) and flow field plates, should conduct electrons and heat, provide mechanical support for the
membrane and CLs and transport the reactant gases while removing the electrochemically produced liquid water.

- **Flow field plates (FFP):**

  The flow field plates contain channels which must ensure the distribution of gas over the whole cell active area. Simultaneously, the channels need to collect and remove the water and electrons need to be gathered by the plates. Various types of flow field geometries can be used, such as straight parallel, interdigitated or serpentine flow channels\(^{19}\). The differences in design offer the possibility to facilitate one transport mode over the other (for example convection over diffusion in the case of interdigitated flow fields).

### 1.2.3 Electrochemical reactions

The electrochemical reactions happen at the catalyst layers (CLs) on both anode and cathode compartments. At the anode, the hydrogen is oxidized to produce protons and electrons. This reaction is known as hydrogen oxidation reaction (HOR) and can be written as:

\[
H_2 \rightleftharpoons 2H^+ + 2e^- \tag{1.1}
\]

Meanwhile, the oxygen is reduced at the cathode side according to the oxygen reduction reaction (ORR), written as:

\[
0.5 O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O \tag{1.2}
\]

Therefore the overall reaction equation can be written as:

\[
H_2 + 0.5 O_2 \rightleftharpoons H_2O \tag{1.3}
\]

The protons generated at the anode are transported to the cathode via the membrane. The electrons travel through an external circuit from anode to cathode, so the membrane needs to block the electrons from flowing across. Additionally, the polymeric membrane needs to be impermeable to gases. If a sufficient gas flow permeates through the membrane, the durability is reduced (by peroxide production) and Faraday’s efficiency is diminished. While the HOR has facile kinetics and virtually does not contribute to the voltage losses, the ORR has a very sluggish kinetics contributing notably to performance losses. A very remarkable fraction of research in electrochemical engineering is being carried out in the framework of improving ORR\(^{20}\).
1.2.4 Thermodynamics

The thermo-neutral fuel cell voltage \( U_{th}^0 \) can be calculated based on the standard reaction enthalpy \( \Delta H_r^0 \) as:

\[
U_{th}^0 = -\frac{\Delta H_r^0}{zF} \approx 1.48 \, V
\]  (1.4)

where \( z \) refers to the number of exchanged electrons and \( F \) is the Faraday constant (96 485 A\cdot s\cdot mol\(^{-1}\)), resulting in the total amount of energy released by the reaction. 25°C, 1 bar and an activity of 1 are the standard conditions in electrochemistry. However, entropic losses are accounted for in the definition of Gibbs, \( \Delta G_r^0 \), free energy as:

\[
\Delta G_r^0 = \Delta H_r^0 - T \, \Delta S_r^0
\]  (1.5)

where \( T \) is the temperature and \( \Delta S_r^0 \) is the standard reaction entropy. Again, considering standard conditions, we can calculate the reversible cell voltage \( U_{rev}^0 \) as:

\[
U_{rev}^0 = -\frac{\Delta G_{rev}^0}{zF} \approx 1.23 \, V
\]  (1.6)

which represents the useful energy produced by the electrochemical reaction.

The thermodynamic fuel cell efficiency, \( \varepsilon \), is the ratio of the amount of useful energy over the total released energy:

\[
\varepsilon = \frac{\Delta G_r^0}{\Delta H_r^0} = 0.83
\]  (1.7)

Under standard conditions, a thermodynamic efficiency of 83% is obtained. It should be mentioned that all thermodynamic variables values herein used refer to liquid H\(_2\)O.

In all previous calculations we have assumed standard conditions. However, in practical PEFCs operation, different temperatures and activities (i.e. gas partial pressure) can be used. The reversible fuel cell voltage can be written generally as:

\[
U_{rev} = -\frac{\Delta G_{rev}(T)}{zF}
\]  (1.8)

The dependence on temperature for reaction enthalpy and entropy needs to be considered. In order to calculate a cell voltage which accounts for the prevailing deviations of reversible voltage the Nernst equation needs to be used. This equation links the thermodynamically-given cell voltage with the cell voltage under standard conditions, temperature, activity and reaction quotient:
\[ U_{rev}(T, P) = U_{rev}(T) - \frac{RT}{zF} \ln \left( \frac{a_{H_2}O}{a_{H_2}a_{O_2}^{0.5}} \right) \]  

(1.9)

where \( R \) is the universal gas constant (8.314 J·K\(^{-1}\)·mol\(^{-1}\)) and \( a_i \) is the activity of reactants and product. For gaseous components, the activity can be linked to the partial pressure by:

\[ a_i = f_i \frac{p_i}{p^*} = f_i y_i \frac{p}{p^*} \]  

(1.10)

where \( f_i \) is the fugacity coefficient and an measure for deviations of ideality, \( p_i \) is the partial pressure of the gas \( i \), \( y_i \) is the molar fraction of gas \( i \) in the gaseous mixture and \( p^* \) is the standard pressure (1 bar). For simplicity, if we assume that the gas behaves as ideal gas (fugacity of 1), for \( T = 70°C \) and \( p = 2 \) bar\(_{abs} \) and an air-fed cathode (\( c_{O_2} = 0.21 \)), a value of \( U_{rev} = 1.19 \) V is obtained.

On top of that, the practical operation of PEFC results in additional losses which will be described in the following section (1.3).

### 1.3 Voltage loss mechanisms

In the previous section, the most relevant fuel cell voltages were derived under conditions of thermodynamic equilibrium. When the PEFC is under operation, an electrical current is produced leading to deviations with respect to this ideal condition. In order to compare the performance of different PEFCs by means of cell size, the total cell current \( (I) \) is often divided by the cell active area \( (A) \), resulting in the current density, \( i \):

\[ i = \frac{I}{A} \]  

(1.11)

The classical diagnostic used to characterize PEFC performance is the so-called polarization or \( V/i \) curve (Figure 1.4), where the cell voltage is plotted versus the current density. In galvanic cells, such as PEFCs, the actual voltage obtained is lower than the voltage under thermodynamic equilibrium. This deviation is captured by the concept of overpotential, \( \eta \), as follows:

\[ \eta = U_{rev}(T, P, a_i) - U^{i=0}(T, P, a_i) \]  

(1.12)
In PEFCs, the overpotentials arising during operation can be classified into three types (Figure 1.4): activation or charge transfer overpotential ($\eta_{CT}$), ohmic overpotential ($\eta_\Omega$) and mass transport or concentration overpotential ($\eta_{MT}$). Each overpotential will be described in the following subsections. The actual cell voltage ($U_{FC}$) at any point of time is therefore given by:

$$U_{FC} = U_{rev} - \eta_{CT} - \eta_\Omega - \eta_{MT}$$  \hspace{1cm} (1.13)

In practice, $U_{rev}$ is not reached even under open circuit conditions for various reasons, such as reactant crossover through the membrane and the mixed potential formed on the cathode involving side reactions such as Pt oxidation. A reduced cell voltage is obtained in absence of current, usually in the range of 0.9-1.1 V depending on cell construction and materials. This voltage is referred to as open circuit voltage, $U_{OCV}$.

### 1.3.1 Charge transfer overpotential

The charge transfer overpotential, $\eta_{CT}$, is related to the electrochemical kinetics. In other words, it is linked to the energy barrier between the oxidized and reduced species.
The relationship between the current density and charge transfer overpotential is given by the Butler-Volmer equation, which is one of the most fundamental relationships in electrochemical kinetics. For the anode \( (i_{an}) \), where the HOR reaction takes place, the equation is:

\[
i_{an} = i_{an}^+ + i_{an}^- = i_{0,HOR} \exp \left( \eta_{CT,HOR} \frac{\alpha_{HOR} F}{RT} \right) + i_{0,HOR} \exp \left( \eta_{CT,HOR} \frac{\alpha_{HOR} F}{RT} \right) \tag{1.14}
\]

while at the cathode \( (i_{ca}) \), where the ORR occurs:

\[
i_{ca} = i_{ca}^+ + i_{ca}^- = i_{0,ORR} \exp \left( \eta_{CT,ORR} \frac{\alpha_{ORR} F}{RT} \right) + i_{0,ORR} \exp \left( \eta_{CT,ORR} \frac{\alpha_{ORR} F}{RT} \right) \tag{1.15}
\]

In this equations \( i_{i}^+ \) and \( i_{i}^- \) refer to the current density in the anodic and cathodic direction (oxidation and reduction) for each of the half-cell reactions. This should not be mistaken with the anode and cathode compartments, since it indicates both directions of a reversible reaction. \( \alpha_{i}^+ \) and \( \alpha_{i}^- \) are the so-called charge transfer coefficients. The parameters \( i_{0,i} \) represent the exchange current density for each reaction. The exchange current density depends on the type of reaction, activity of the catalyst used, active surface available per unit of geometric area, temperature and partial pressure of the reactants. Large values of \( i_0 \) for a given reaction minimize the charge transfer overpotential. If air is used instead of pure oxygen, the \( i_0 \) would decrease, leading to an increase in charge transfer overpotential.

Due to the sluggish nature of the ORR, in PEFCs it is mostly considered that \( \eta_{CT,ORR} \) dominates. To give some context, the exchange current density of the HOR on a flat Pt metal surface is \( i_0 \sim 10^{-1}-10^{-3} \text{ A cm}^{-2} \) (at ambient temperature and highly dependent on pH)\(^2\), while the ORR on the same surface has a value of \( i_0 \sim 2.5 \cdot 10^{-8} \text{ A cm}^{-2} \). Is can therefore be assumed that the total cell charge transfer overpotential is linked to the cell current density as according to:

\[
i = i_{ca} = i_{ca}^+ + i_{ca}^- = i_{0,ORR} \exp \left( \eta_{CT,ORR} \frac{\alpha_{ORR} F}{RT} \right) + i_{0,ORR} \exp \left( \eta_{CT,ORR} \frac{\alpha_{ORR} F}{RT} \right) \tag{1.16}
\]

When \( i_{ca}^- > 10 i_{ca}^+ \), which should be the case because the reaction happens in the cathodic direction, then the Butler-Volmer equation can be simplified to:

\[
\eta_{CT} = \frac{RT}{\alpha_{ORR} F} \ln \left( \left| \frac{i}{i_{0,ORR}} \right| \right) \tag{1.17}
\]

This equation is normally re-written as the well-known empirical Tafel equation:

\[
\eta_{CT} = a + b \log(i) \tag{1.18}
\]
By performing a linear fit of $\eta_{CT}$ versus $\log(\delta)$, the parameters $a$ and $b$ can be obtained. These are normally obtained experimentally and serve to compare the activity of different catalysts for a given electrochemical reaction.

### 1.3.2 Ohmic overpotential

The ohmic overpotential arises from ionic and electronic resistance of conductors. In PEFCs, the resistance to conduct ions across the polymer electrolyte membrane and the ionomer present in CLs are the two contributions of the ionic resistance ($r_{ion}$), while the electrons need to be transported through the different layers (CL, MPL, GDL, FFP) which contribute to the electronic resistance ($r_{electron}$). Logically, the thinner the conductors, the lower the resistance value would be. That is the reason why research targets the implementation of thinner membranes. An important contribution to the ohmic overpotential is due to contact resistances ($r_{contact}$), which are resistances occurring at the interface between two different layers, for example, CL-GDL (or CL-MPL) and GDL-FFP. Normally, larger cell compressions are used to minimize the contact resistance.

$$\eta_\Omega = (r_{ion} + r_{electron} + r_{contact})i = ri \quad (1.19)$$

Equation 1.19 seems to point to a linear increase of $\eta_\Omega$ over current density (Ohm’s law). However, in practice this in not observed because, for example, the electrochemically produced water hydrates the membrane and ionomer, hence decreasing $r_{ion}$.

### 1.3.3 Mass transport overpotential

As previously mentioned, the use of air instead of pure oxygen results in an increase of charge transfer losses and a reduction of the Nernst potential. Apart from these contributions, the concentration of oxygen at the electrode is reduced due to mass transport limitations and an additional overpotential arises, known as mass transport overpotential, $\eta_{MT}$. It can be calculated as:

$$\eta_{MT} = \left(1 + \frac{1}{a_{\text{O}_{2,\text{RR}}}}\right) \frac{RT}{zF} \ln \left(\frac{c_{O_{2,\text{ref}}}}{c_{O_{2}}^S}\right) \quad (1.20)$$

Where $c_{O_{2}}^S$ is the local oxygen concentration at the electrode’s surface and $c_{O_{2,\text{ref}}}$ is the reference concentration (0.21 for air). It is then obvious that a reduction in $c_{O_{2}}^S$ leads to increase in mass transport overpotential. There are various mechanisms at different
levels influencing the final oxygen concentration at the electrode. These can be listed as follows:

- In a technical size cell oxygen gets depleted along the flow field channel towards the outlet, hence the sections near the outlet suffer from strong mass transport losses. In this work differential cells have been used with the objective of eliminating this effect. Differential cells use elevated flow rates and small sizes to mimic the conditions in one section of a larger technical cell.

- The diffusive transport is driven by a concentration gradient. If the pores are sufficiently large, the probability of gas molecules colliding between themselves is much greater than the collision between molecules and pore walls. This is known as “bulk diffusion” and is relevant in GDL pores and interfaces. More details on bulk diffusion are given in 1.4.5.

- If, however, the pores are small enough, the probability of gas molecules colliding with pore walls becomes dominant and we talk about Knudsen diffusion. In essence, if the mean pore diameter, $d_{pore}$, is in the range of the mean free path of the gas molecules, which is $<35$ nm for $\text{O}_2$ at 2 bar of absolute pressure, then this mechanism becomes relevant. Knudsen diffusion is only dependent on partial pressure and does not change with the inert gas carrier.

- The last mechanism, known as thin film diffusion, is based on the diffusion of gas molecules throughout a thin film of liquid and ionomer. In PEFCs, this is related to the diffusive transport within the ionomer covering the electrodes in the catalyst layers.

In this project we develop novel gas diffusion layers with the goal of minimizing the mass transport overpotential. In particular, the bulk diffusive transport is expected to be improved by a better water management in the GDLs. Let us consider a simplified case in which one-dimensional diffusive transport occurs through the different layers in the direction perpendicular to the membrane plane. Combining Faraday’s law and the 1st Fick law (stationary) the current density is calculated as:

$$i = zF D_{rel} \left( \frac{c_{O_2,ref}^S - c_{O_2}^S}{\delta} \right) \quad (1.21)$$

Where $D_{rel}$ is the relative diffusivity and $\delta$ is the thickness of the diffusion layer. $D_{rel}$ is a function of the binary diffusion coefficient of the gas, the microstructure of the material and the water content. This is described in further detail later (1.4.5). A very common parameter discussed in the literature is the limiting current density, $i_{lim}$:

$$i_{lim} = zF D_{rel} \frac{c_{O_2,ref}^S}{\delta} \quad (1.22)$$
Introduction

It has been assumed that the oxygen is completely depleted at the electrode’s surface ($c_{O_2}^S = 0$). This represents the limiting case for mass transport. Experimentally, $i_{lim}$ is obtained by using artificially diluted oxygen concentrations (typically in the range 0.01 – 0.05)\(^{[24]}\) in nitrogen and provides a useful parameter to compare how different GDL materials influence the mass transport. It should be mentioned that the two-dimensional calculation taking into account the differences between rib and channel significantly increases the complexity of the problem.

1.4 Water management in PEFCs

Extensive literature has focused on the topic of water management. The following subsections provide an explanation of the impact that water has in the different PEFC components and then discusses the main transport mechanisms.

1.4.1 Impact of the water

The impact of water in the different PEFC components is:

- **In the membrane:** water is needed to hydrate the polymer structure. Higher water contents increase proton conductivity and therefore reduce ohmic overpotentials\(^{[23]}\). A good membrane should be able to perform well at low water contents as well.

- **In the CLs:** the ionomer should be hydrated to conduct protons and favor oxygen diffusion. Excessive amounts of liquid water can block active surface, which results in mass transport losses. On top of that, the water vapor partial pressure reduces the partial pressure of oxygen and therefore increases the charge transfer overpotential. Additionally, the reversible cell voltage will be affected by a change in activity and therefore there would be an additional voltage loss.

- **In the MPLs:** while many reports have focused on the impact that MPLs have on PEFC performance, the role of the MPL is terms of water management in not fully understood. Due to the hydrophobicity and small pore size, it appears unrealistic that they saturate with liquid water and therefore the pores should remain rather free for gas transport, and the large cracks (or imperfections) seem to fill preferentially\(^{[26]}\).

- **On the GDLs:** the presence of liquid water in the GDLs can only have a negative influence on performance. It blocks pores and therefore increases the resistance to diffusive transport. This will be discussed in more detail in section 1.4.5.
- **On the channels**: liquid water droplets collect on external surfaces of GDLs towards the flow field channels and need to be removed by the gas stream. If excessive accumulation occurs due to, for example, large retention forces from GDL surfaces and roughness, the gas flow distribution (either channel-to-channel or cell-to-cell) can be impaired\[21\].

### 1.4.2 Oxygen and water transport in the cathode GDL

Since this PhD work focuses on developing GDLs with improved transport properties for the cathode, in this subsection the main transport modes will be discussed to set the basis for the coming subsections:

- **Water**: the water produced in the CLs needs to be removed. In liquid phase, the capillary transport in considered the main driving force for water to break through the GDL and form low pressure pathways for the water to leave the cell\[28\]. Once a pathway is formed, then the effective permeability of the created liquid network will determine the pressure drop. On top of that, due to the PEFC operating temperature (60-90°C), an important fraction of the water is in vapor phase. Water vapor can be transported by diffusion driven by a concentration gradient, which can be present either in unsaturated conditions or in the presence of a temperature gradient. Since humidified gases are fed through the gas channels, this interplay is rather complex and predictions cannot be made without experiments or numerical simulations. In short, the evaporation and condensation of water in the GDL has an important influence in the water redistribution.

- **Oxygen**: the oxygen travels from the flow field channels to the CLs by a combination of convection and diffusion. Convection is favored if interdigitated flow fields are used, for example, and under the channel areas where the flow velocity vector can push the gas towards the GDLs. When air is used diffusion dominates the transport resistance since oxygen needs to diffuse into the mixture of nitrogen, water vapor and minor traces of other gases.

### 1.4.3 Capillarity and wettability

Capillarity refers to the ability of a liquid to flow in narrow spaces without the assistance of external forces. For example, absorbent paper wicks the water and sap ascends in plants’ roots due to capillary actions, even against gravitational acceleration. If we assume that liquid is the wetting phase and gas is the non-wetting phase, the capillary pressure $P_C$ can be defined as:
\[ P_C = P_G - P_L \]  

(1.23)

where \( P_C \) is the pressure in the gas and \( P_L \) is the pressure in the liquid. On the other side, the Young-Laplace equation provides a relationship between the capillary pressure and the curvature of the interface between liquid and gas interfaces [29]:

\[ P_C = 2\gamma \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \]  

(1.24)

where \( \gamma \) is the surface tension of the liquid-gas interface and \( r_1 \) and \( r_2 \) are the principal radii of curvature. In the simplified case of a cylindrical geometry, the capillary pressure can be calculated as:

\[ P_C = -\frac{2\sigma \cos\theta}{r} \]  

(1.25)

where \( r \) is the cylinder radius and \( \theta \) is the contact angle which is a variable describing how the solid is wetted by the liquid. This is discussed in further detail in the next paragraphs. It should be noted that the GDL geometry is rather complex and therefore capillary pressure cannot be successfully modelled as a straight cylindrical tube. In order to provide a more realistic description of the physical phenomena, a modified model was developed and will be presented in Chapter 6.

Due to the influence of the contact angle on the capillary pressure, the next lines are dedicated to describe the fundamentals of wettability on flat and rough surfaces. Let us imagine a perfectly flat, horizontal and dry solid surface, on which a droplet of a liquid is placed. As shown in Figure 1.5.a, a contact angle, \( \theta \), is defined between the solid and liquid interface. Hydrophilic surfaces result in \( \theta < 90^\circ \) while hydrophobic surfaces result in \( \theta > 90^\circ \). It is common to talk about surfaces with intermediate (or neutral) wettability when \( \theta \approx 90^\circ \). The definition of a certain contact angle is given by the interplay between the three contacting interfaces. The Young’s equation relates the equilibrium contact angle as follows:

\[ \gamma_{SG} - \gamma_{SL} - \gamma_{LG} \cos(\theta) = 0 \]  

(1.26)

Where \( \gamma_{SG} \), \( \gamma_{SL} \) and \( \gamma_{LG} \) are the surface tension of the different interfaces (solid-gas, solid-liquid and liquid-gas). The surface tension is the elastic tendency of an interface to acquire the smallest possible surface area. While this theory is valid for ideally flat substrates, solids with rough surfaces often exhibit unexpected wetting behaviors. An apparent contact angle (or external contact angle), \( \theta_{app} \), is defined on the external
surface which can be significantly different to the intrinsic (or internal) contact angle, \( \theta_{int} \), defined between the internal solid and liquid interfaces (Figure 1.5.6).

\[ \cos \theta_{app} = r_f \cos \theta_{int} \]  \hspace{1cm} (1.27)

where \( r_f \) is the roughness factor, defined as the ratio between the actual surface area of the material and its geometrical area. The Wenzel regime indicates that intrinsically hydrophilic materials show apparent contact angles of a lower value and that an intrinsically hydrophobic material holds droplets with larger apparent contact angles.

The other theory, known as Cassie-Baxter theory or heterogeneous wetting regime, assumes that gas (or the gas partially saturated with liquid’s vapor) remains trapped in the surface asperities. The apparent contact angle can be calculated as:
\[ \cos \theta_{\text{app}} = f_1 \cos \theta_{\text{int}} - f_2 \] (1.28)

where \( f_1 \) is the total surface of the solid-liquid interface and \( f_2 \) is the total surface of the air-liquid interface. An important point to mention is that is this case – and contrary to the description by the Wenzel theory – it is possible that an intrinsically hydrophilic material results in an apparently hydrophobic surface. Further details on the Cassie-Baxter theory can be found in Chapter 4.

In summary, this subsection illustrated the difficulty on understanding wettability on porous (rough) materials. An important remark should be made: the capillary pressure (equation 1.25) depends on the intrinsic contact angle. GDLS are highly porous materials and so of a heterogeneous nature (composed of carbon fibers, coating and binders). It is therefore challenging to obtain conclusive values of intrinsic contact angles for GDLS experimentally. Chapter 2 discusses our attempts to obtain internal contact angles for GDLS (section 2.3.3).

1.4.4 Permeability

The fluid flow through a porous material can be described by the Darcy law:

\[ \vec{v} = -\frac{K}{\mu} \nabla p \] (1.29)

where \( \vec{v} \) is the velocity vector, \( K \) is the absolute permeability, \( \mu \) is the viscosity of the fluid and \( \nabla p \) is the pressure gradient. The permeability is a material-specific property measuring the resistance against flow through that material and it normally is a function of porosity and some particle length. The Carman-Kozeny equation correlates material properties with absolute permeability \([32, 33]\):

\[ K = \frac{d_C^2 \varepsilon^3}{16k_{CK}(1-\varepsilon)^3} \] (1.30)

where \( \varepsilon \) is the porosity, \( d_C \) is a characteristic particle length and \( k_{CK} \) is a constant that needs to be determined experimentally for a given material. In the case of GDLS, \( d_C \) is represented by the fiber diameter. The equation shows that larger pores increase the permeability and therefore reduce the resistance to flow. If isotropic media are used, \( K \) is a scalar. However, in anisotropic materials, such as most of GDLS \( K \) must be represented as a tensor.

Liquid and gas phase coexist in the GDLS during PEFCs operation. A relative permeability for a given phase, \( P \), can be defined following the nomenclature of Gostick\([34, 35]\) as:
\[ K_{\text{rel}, P} = \frac{K_{\text{eff}, P}(Sp)}{K} \] (1.31)

Where \( K_{\text{rel}, P} \) is the relative permeability of phase \( P \), \( K_{\text{eff}, P} \) is the effective permeability in presence of another phase of phase \( P \) and \( sp \) is the saturation of phase \( P \), which varies between 0 and 1. Empirical correlations for relative permeability of this form have been extensively published in fuel cell literature:

\[ K_{\text{rel}, P} = S_P^a \] (1.32)

Where \( a \) is a constant, usually taken as \( \sim 3 \) in the modelling literature. It should be mentioned that the experimental measurements of relative permeability in GDLs are rather difficult and are based on \textit{ex situ} test configurations. Recently, various modelling approaches, such as Lattice Boltzmann method (LBM)\cite{36} and Pore Network Modelling (PNM)\cite{37}, are being used to extract relative permeabilities from reconstructed or artificially created GDL microstructures.

1.4.5 Effective and relative diffusivity

In a porous GDL, the effective diffusivity refers to the diffusion of a species \( \Lambda \) (oxygen) through a species \( B \) (nitrogen in the air mixture) within the substrate’s pores. It is different from the diffusivity of \( \Lambda \) through \( B \) in open space and can be written as:

\[ D_{\text{eff}} = D_{AB} \frac{\varepsilon}{\tau} \] (1.33)

where \( D_{\text{eff}} \) is the effective diffusivity in a dry structure, \( D_{AB} \) is the binary diffusion coefficient, \( \varepsilon \) is the porosity and \( \tau \) is the tortuosity.

As previously discussed, in GDLs during cell operation the presence of water hinders diffusive transport. This is captured by the relative effective diffusivity, \( D_{\text{rel}, P} \), which is defined as:

\[ D_{\text{rel}, P} = \frac{D_{\text{eff}, P}}{D_{\text{eff}}} \] (1.34)

where \( D_{\text{eff}, P} \) is the effective diffusivity through phase \( P \), which varies with the saturation between 0 and 1. As with relative permeability, empirical correlations have been obtained for different GDL materials of the form:

\[ D_{\text{rel}, P} = (1 - s_L)^b \] (1.35)

where \( s_L \) is the saturation of pores with liquid and \( b \) in an exponent found experimentally for different GDLs. Various studies have targeted the extraction of this
coefficient both with experiments and simulations\textsuperscript{38-40}. For example, Rosen et al. experimentally obtained $b$ values of 2.15 and 3.05 for the in-plane and through-plane directions, respectively\textsuperscript{41}.

1.5 The gas diffusion layer

The GDL is a three-dimensional porous material composed of carbon fibers arranged in different fashions. To avoid misunderstandings, we refer in this thesis to \textit{diffusion layers} as a bi-layer material composed of GDL and MPL. As in this work we will mostly discuss and investigate GDLs, the reader should keep in mind that we are talking about a mono-layer substrate of high porosity and large average pore size (10-40 μm). As shown in Figure 1.6, the GDL has attracted enormous attention from research in the last 15 years, with around 3500 publications up to date ($\sim$300 publication/year in the last 5 years) and a continuous growth, showing the key role that the material plays in the success of PEFC technology. The next subsections discuss GDL functionalities, commercially available GDL types and closes with the industrial production of GDLs.

![Figure 1.6 – Cumulative number of publications concerning GDLs and MPLs since 1998. Information obtained from Scopus, access date: 13.09.2016.](image)

1.5.1 Functionalities

In this subsection the main functions provided by the GDLs will be described, together with the corresponding required material properties:

- GDLs should distribute the reactant gases from the FFP channels towards the CLs where the electrochemical reactions take place. To do so, a large open
porosity and low tortuosity favor high values of effective diffusivity and effective gas permeability. As previously described (section 1.4) these parameters are strongly affected by the water content and its location.

- Simultaneously, GDLs need to remove the liquid water produced by the electrochemical reactions to avoid cell flooding and hinder gas transport. As already mentioned, the water management is very complex and optimal gas/liquid transport characteristics most probably cannot be provided by the common materials. As a general rule, large porosity and hydrophobic internal surfaces would favor water removal. However the transport of water is determined by a complex interplay of various phenomena, including evaporation/condensation, capillary transport and permeation through already formed pathways.

- They should conduct electrons from the CL (or MPL) to the FFP. Generally, this is not regarded as a major issue since electrical conductivity of carbon fibers is rather high ($\sigma > 1000$ S·cm$^{-1}$ [42]). However, the presence of hydrophobic coatings which are electrical insulators can significantly impact GDL electrical conductivity [43]. The contact resistance is an important issue to control in order to efficiently transport the electrons. In this context, intimate contact between layers (CL-MPL, CL-GDL, MPL-GDL and GDL-FFP) is crucial. The compression strongly impacts the contact resistance and, logically, greater compressions reduce the contact resistance [43, 44].

- GDLs should also effectively conduct heat. Large amounts of heat are produced by the electrochemical reactions at the CLs, which needs to be removed to ensure operation at reasonable temperatures (i.e. 80°C). If a material is a good electrical conductor, it will generally be a good thermal conductor. Such is the case for GDLs and similar trends have been reported in the literature [45-47].

- It provides mechanical support for the PEM and CL and cushions the different compression cycles that can appear from cell building or due to expansion and contraction of the membrane during the hydration cycles [48, 49].

1.5.2 Composition and types

Most of the literature published in the field of GDLs for PEFCs involves the use of carbonaceous materials (i.e. carbon fibers) as skeleton of the GDL. Few reports have been published investigating the use of metal meshes, sintered metals or foams and some silicon based materials [50]. While these approaches are interesting and may inform other important fields such as polymer electrolyte water electrolysis, it appears difficult to overcome the advantages of carbon as a substrate, especially regarding stability,
manufacturability and, most importantly, cost. The carbonaceous skeleton is often coated with a hydrophobic polymer to increase water repellency and reduce flooding. Polytetrafluoroethylene (PTFE) is the most commonly used material (TEFLON®), followed by fluoroethylene-propylene (FEP). Some manufacturers also include abundant amounts of binders. Binders usually impart mechanical stability by “gluing” fibers together, but they are also used to increase the electrical and thermal conductivity. Figure 1.7 shows various examples of commercially available types of GDLs.

Figure 1.7 – SEM images of the following GDL materials: (a) Toray TGP-H-060 uncoated; (b) SGL 24BA with ~5% PTFE; (c) Freudenberg H1410 uncoated; (d) Freudenberg H2315 I2C6 with ~10% PTFE; (e) Quintech cloth CC CC060; (f) Higher magnification of CC CC060 showing the carbon fibers orientation.

According to the way in which they are manufactured, commercially available GDLs can be divided in two main groups: woven and non-woven materials. The former, also referred to as carbon cloths, are typically prepared by weaving carbon or graphite fibers (Figure 1.7.e and 1.7.f). Vendors of cloths include AvCarb® and Quintech[50]. The non-woven substrates can be further divided into carbon papers and carbon felts. While carbon papers are prepared from slurries, the processing of carbon felts involves the use of felting machines allowing greater control over three-dimensional orientation of fibers. Carbon papers are mostly chosen over felts for PEFCs applications, while felts are extensively used in redox flow batteries. Toray Industries produces GDLs with rather graphitized carbon fibers, low amounts of binder, high porosity (~80%) and rather narrow pore size distribution (Figure 1.7.a). SGL Carbon Group sells various types of carbon papers with a characteristic “flake-like” binder covering a notable fraction of the
material, also large porosity (75-90%) and rather broad pore size distributions (Figure 1.7.b). Freudenberg commercializes GDLs which seem to be shaped as felts, even though many reports found in literature categorized them as papers. While different degrees are available, these GDLs feature flexibility, narrow pore size distribution and small average pore diameter, as compared to the other substrates (Figure 1.7.c and 1.7.d). In this PhD work, carbon papers/felts purchased from these three suppliers have been used. Other vendors of non-woven materials include Spectracorp and Avcarb®.

1.5.3 Industrial production

Few public reports have covered the details of industrial production of GDLs for PEFCs. Very recently, SGL group has published a white paper[51], in which they illustrate the different processing steps required to manufacture state-of-the-art diffusion layers. As can be seen in Figure 1.8 the final MPL coating step is also included in the process. Based on the aforementioned diagram and other information found in books[52], we could list the main synthetic steps as follows:

(I) The starting point is the preparation of a precursor and the formation of precursor fibers by extrusion. Generally polyacrylonitrile is the material of choice, but cellulose fibers have also been used. It is important to mention that in the manufacturing of cloths (and some felts) the precursor may already be shaped and woven from this very first step. In most of the cases, the precursor is oxidized and carbonized as independent filaments and post-processed.

(II) A series or thermal oxidative steps brings the material up to ~1 000°C to convert them into a lower molecular weight form of the original precursor.

(III) Afterwards, fibers undergo a series of carbonization steps at higher temperatures which lead to removal of the remaining hydrogen, nitrogen and oxygen atoms. Carbonized fibers are chopped to the desired length. This step influences the final pore size distribution.

(IV) When needed, the fibers are impregnated with a resin to bind the network and improve the mechanical integrity of the substrate. A classical phenolic resin is Bakelite®, but also polymeric binders are used.

(V) The slurry with carbonized fibers and binders is compacted and compressed to form the paper. This step permits control of paper thickness, density and porosity.
(VI) The already formed paper undergoes further treatment steps in order to cure the binder, carbonize and, when desired, graphitize the remaining fibers. The graphitic crystallinity is mainly determined by the type of precursor and the temperature and keeps increasing up to 3 000°C. Generally, GDLs for PEFCs are treated at a temperature range of 1 700-2 000°C.

(VII) The carbon paper is then coated with the hydrophobic polymer. This is done using a water-based dispersion that contains small particles (~200 nm) of PTFE (or FEP) and surfactants to ensure good distribution and complete wetting of the substrate. A subsequent thermal treatment allows removing of the solvents and surfactant and finally sintering the polymer. The concentration of solids in the dispersion as well as the thermal treatment influence the final coating load and distribution.

(VIII) Further steps include the application of microporous layers or further treatments to optimize GDLs properties. Our synthesis method to develop GDLs with patterned wettability would involve the addition of some additional steps (irradiation, reaction and cleaning) to be integrated at this point of the flow diagram. This will be discussed in further detail in section 1.7.4.
1.5.4 Costs

It stands to reason that GDL cost needs to be minimized to guarantee the success of PEFCs technology. Some PEFCs components, such as catalysts layers and membranes, are inherently expensive due to the use of precious metals, the scarcity of these metals and complexity of the production process. GDLs are one of the PEFC component made of abundant, cheap and easy to manufacture components, making possible a lowering in the GDL cost thanks to the economy of scale. This is well represented in Figure 1.9, where it can be seen that the proportional cost of GDLs represents 20% of the stack cost if 1 000 units/year are produced, but drastically decreases to only 5% if 500 000 units/year would be produced. The degree of automatization by, for example, creating continuous roll-to-roll lines would explain this decrease in relative cost.

If we assume an annual production rate of 500 000 units/year, then the likeliest estimated GDL cost is \(4.08 \text{ \$/m}^2\) \(^{[10]}\). This value will serve as basis for calculating the expected additional cost due to the implementation of our technology (section 1.7.4).

![Figure 1.9](image)

**Figure 1.9** – Breakdown of the estimated stack (80 kW) cost (year 2015) for two different production rates: (a) 1 000 units/year; (b) 500 000 units/year. Adapted from Ref\(^{[10]}\).

1.6 Optimized gas diffusion layers: a literature review

Over the last 15 years, many groups all over the world have studied the impact of different GDLs on fuel cell performance and applied diverse treatments to improve the water management. The main approaches will be described in the following paragraphs, divided in whether they are based on modifications over the complete substrate or in localized modifications.
1.6.1 **Improvements based on overall treatments**

The presence of an optimal coating load (PTFE and FEP) has been reported for different GDL materials\[53-55\]. The through-plane coating distribution as a function of treatment conditions and its effect on performance have been investigated and it was found that vacuum dried coating distributed more homogenously leading to a reduced gas permeability\[56-60\]. The main disadvantage related to the “dipping” method to apply the polymeric coating is the little control over formation of agglomerates. Ideally, a well-distributed thin hydrophobic coating should cover most of carbon fiber surfaces. In this context, two recently developed approaches have been published. Thomas et al. used electrochemical reduction of diazonium salts in liquid phase to produce thin layers of hydrophobic molecules covalently bonded on the carbon fiber surfaces. Using SGLs materials, they demonstrated significant improvements of performance under high gas relative humidity conditions\[61\]. Another approach has been published by Van Nguyen et al. and is based on direct fluorination. In this method, fluorine gas at elevated temperatures is flown throughout the GDLs and reacts with carbon surfaces to create a diversity of molecules creating thereby hydrophobic surfaces\[62, 63\]. While the use of these modified GDLs leads to performance improvements with respect to baseline materials, they still do not provide optimized gas/liquid transport characteristics since the water transport relies on stochastic microstructural features and coating distributions. In order to engineer pre-designed preferential locations for the water and gases to flow through, methods based on local modifications need to be used. A review on the main published approaches is presented in the following subsection.

1.6.2 **Improvements based on localized modifications**

To the best of the author's knowledge, the first published approach to channel water within the GDL was made by Gertiesen et al. and followed by other groups\[64-66\]. The authors perforated GDLs (using laser or mechanical methods) with different holes diameter under the flow field channel areas. Logically, the creation of large “pores” forces the water to flow preferentially through them. On top of that, it was demonstrated that a higher oxygen content existed in the adjacent regions of the perforations when a laser was used. Reduced mass transfer resistance was found under some operating conditions; however, the method suffers from design limitations. While the perforation approach is based on physically modifying the GDL microstructure, other approaches are based on customizing the wettability at a local scale.

Utaka et al. presented a hybrid porous material composed of an arrangement of two different porous media with different wettability\[67-70\]. Using an ex situ diffusivity rig, it
was found that oxygen diffusivity was increased by using hybrid materials. Years later, the same group proposed the use of locally coated (PTFE) GDLs. Again, oxygen diffusivity was improved and the water was imaged using X-ray radiography showing a not so clear segregation of the water between the two domains. While the potential of these hybrid materials to improve gas transport was clearly demonstrated, the production method offers limited design flexibility and presents difficulties to scalability. Finally, a few additional technologies can be found in protected literature. Mekala et al. patented a method to modify the external GDL surfaces using plasma to thereby create oxygen-rich molecules[21]. Since plasma is a surface sensitive technique, it is expected that these materials would have hydrophilic external surfaces but the inner surfaces remain untreated. Another recent patent from SGL Carbon Group involves the addition of solid oxide nanoparticles to the GDL to generate hydrophilic domains[22]. The main concern is related to the lack of covalent bonds, which may impact long-term durability.

1.7 Our technology: electron radiation grafting of porous materials

While the synthetic method is explained in detail in Chapter 3, this section should serve as an introduction to the technology invented within this project[73, 74]. The general concept and main synthesis steps will be presented, followed by the advantages that this approach offers with respect to previously reported methods and closing by some comments on scalability potential and estimated costs.

1.7.1 The concept

As previously described (section 1.6.2) other approaches targeted the production of GDLs having preferential pathways within the GDL for the liquid water to be transported to the flow channels. The same fundamental idea is targeted with our approach, as shown in Figure 1.10. If water is channeled through dedicated pathways from CLs to FFP channels, then a greater fraction of GDL pores will be free of water and gas transport will be favored. In conventional materials, the transport of water is determined by an interconnected network of pores providing the lowest capillary pressure (larger and less hydrophobic pores) which generally leads to tortuous and dead-ended pathways, consequently forcing the gases to travel longer distances. In other words, the effective diffusivity and permeability of the gas are reduced and therefore mass transport losses increase. The interplay between gas and liquid transport in state-of-the-art conventional materials is therefore un-optimized.
The originality of our approach relies on creating pathways for the water by locally modifying the wettability of the material. This is done by copolymerizing a hydrophilic monomer onto the hydrophobic GDL coating only in the desired regions. Since the average pore diameter of GDLs used in this work is the range of 20-40 µm, we defined 100 µm as the minimum reasonable pattern width target.

A simple estimation illustrates the potential in terms of diffusivity increase by having water confined to selected domains. Let us assume that 1/3 of the area is hydrophilic and that the hydrophilic domains are fully saturated with water. The remaining hydrophobic area (2/3) is empty. Using the following empirical relation for effective diffusivity[41]:

$$ D_{\text{rel}} = (1 - s)^{2.15} $$  \hspace{1cm} (1.36)

and assuming that the water is homogenously distributed in a baseline material ($s=0.33$), the improvement in diffusivity is:

$$ \left( \frac{D_{\text{rel,patterned}} - D_{\text{rel, baseline}}}{D_{\text{rel,baseline}}} \right) \times 100 = 60\% $$  \hspace{1cm} (1.37)

It should be borne in mind that this calculation contains a notable number of assumptions, such as treatment of the problem as mono-dimensional and the complete segregation of water on the hybrid GDL.

### 1.7.2 Synthetic steps

The main steps of the synthetic method are illustrated in Figure 1.11 and will be enumerated here:

1. A hydrophobic coated GDL is used as starting point. This substrate could be a current state-of-the-art commercially available substrate or a plain carbonaceous substrate coated in-house when deemed necessary.
b) The substrate is then irradiated with electrons using blocking masks. An activated material is obtained which can be immediately subjected to the further treatment step or stored at low temperatures (i.e. -80°C) to preserve the radicals.

c) The activated material is brought into a solution containing a hydrophilic monomer and heated to moderate temperature (e.g. 60°C) to initiate the radical polymerization.

d) A final material is obtained with segregated hydrophilic and hydrophobic domains.

A final cleaning step is often required to remove the unreacted monomer and homopolymer formed during the reactions. Incomplete cleaning may lead to low quality materials due to contaminated hydrophobic regions.

1.7.3 Advantages over previous approaches

The main advantages of GDLs with patterned wettability produced by the radiation grafting method can be summarized as:

- There is full flexibility in the pattern design. By changing the blocking mask openings, virtually any pattern can be created.
- The penetration depth of the electrons can be regulated by tuning the energy of the electrons. For example, if only one of the layers of a bi-layer material, such as GDL-MPL, needs to be modified, this could be done by selecting the appropriate energy (Chapter 5).
• The wettability can be tuned by selecting a suitable monomer system and reactions conditions (concentration, solvents, temperature, reaction time, etc.).
• The mechanical, thermal and electrical properties should not be significantly influenced since the carbonaceous skeleton remains unmodified.
• The synthetic method can be realistically scaled-up and integrated into a roll-to-roll processing line, as discussed in the following section.

1.7.4 Scalability potential and additional cost

One of the main advantages of the proposed method is the scaling-up potential due to the possibility of integrating the additional steps in a roll-to-roll process. Let us consider the manufacturing process shown in Figure 1.8 leading to a state-of-the-art GDL. Since the hydrophobic coating and, when required, MPLs have been already included at that point, only three additional steps need to be incorporated in order to manufacture GDLs with patterned wettability (Figure 1.12). An electron beam in the energy range of 100-400 keV needs to be integrated, together with a blocking mask (made of steel). A liquid phase reactor containing a monomer solution in water or other solvent and heated up to 50-70°C is also needed and some final cleaning steps. All these steps can be implemented in a roll-to-roll process without significant modification of the current cycle.

![Figure 1.12 – Proposed manufacturing process. It can be considered a continuation of the current state-of-the-art process shown in Figure 1.8.]

An important point that should be considered is the additional GDL production cost brought by the inclusion of these new processing steps. Let us assume that the estimated GDL cost (4.08 $/m²) is exclusively due to material production costs. The following assumptions are made in order to calculate the incremental cost:

• An electron beam needs to be purchased. They are rather common in industry nowadays and could be acquired from COMET at an approximate cost of 350 000 $/unit. We assume that a 30 cm width GDL roll will be processed which
matches the actual electron beam size. Electricity cost and maintenance are neglected.

- The purchasing of the chemical reactor is another notable contribution to the capital cost. It is important to mention here that the production rate will impact the reactor design. For example, at the current estimated production rate, an approximate of 1 m/min of GDL would be produced if operating 24/7. Consequently, the reaction time and reactor design need to match such a production rate. We will demonstrate in Chapter 4 that rather hydrophilic materials can be obtained after only 10 minutes reaction time, which is the reaction time assumed for this calculation. If the GDL substrate would be conveyed throughout the reaction in a straight line, then a 10 meter long reactor would be needed. Let us assume that a system of rolls can reduce the actual reactor lengths by a factor of 4, leading to a reactor of 2.5 meter length. For the reactor with the corresponding tubes for monomer recirculation, feeding and nitrogen flow, we hypothesize a cost of 300 000 CHF, built in stainless steel. This initial investment (capital costs of reactor and electron beam) will be gradually amortized in 10 years.

- A fuel cell system production rate of 500 000 units/year is considered. If 80 kW systems are built with a total active area of 8 m², then a minimum production rate of 4 000 000 m²/year is required. Let us assume that our production site undertakes 5% of global GDL production, which lead to 200 000 m²/year.

- The most expensive part of the process regarding operational costs comes from the monomers that need to be purchased and will be consumed during the process and the nitrogen that needs to be flushed during reactions. If we assume that the complete open volume (non-solid, $\varepsilon = 0.7$) needs to be filled with monomer solution and a reuse coefficient capturing the fraction of monomer that can be reutilized, then we can calculate the amount of monomer needed per m² of GDL. For the monomers used in this thesis, we have assumed a cost of 1.76 $/kg and 3.00 $/kg for acrylic acid (AA) and N-vinylformamide (NVF)[75, 76], respectively, and reuse coefficients of 0.6 and 0.9 due to larger homopolymer formation in the case of acrylic acid. AA is used diluted in water down to 15%wt. and NVF is used pure.

- The need of carrying out the grafting reaction under low oxygen concentrations required the use of nitrogen flushing. It is difficult to predict the requires nitrogen flow, since it depends on reactor volume, monomer recycling rate and sealing capacity. To give some rough estimate, we assume that 10 Nm$^3$/h are needed with a cost of 0.5 $/Nm^3$ (based on data provided by COMET).
Introduction

- The heat needed to maintain the reactor temperature in the range of 50-70°C can be obtained residually from any other step of the process, such as the carbonization or graphitization ovens.
- The cleaning steps do not lead to a significant cost increase due to the low cost of these solvents (commodities) and the possibility to reuse them.

The amortization of the capital costs (electron beam and reactor) would increase to 0.31 $/m² during the first 10 years. The estimated operational costs are: monomer is 0.015 $/m² for AA and 0.043 $/m² for NVF and 0.21 $/m² for nitrogen. In sum, the additional cost to produce GDLs with patterned wettability during the first 10 years will be 0.53 $/m² if AA is used and monomer and 0.56 $/m² if NVF is used, which translates into an incremental increase of the GDL cost of ~13% and ~14%, respectively. If the modification is used on the cathode side only, and assuming a power density of 1 W/cm² of active area, the incremental cost is in the order of 0.06 $/kW, which is ~0.2% of the ultimate PEFC target cost during the amortization years.

A slight GDL cost increase would be justified if power density is significantly improved. In some detail, if the PEFCs operates more efficiently thanks to an improved water management, the price per kilowatt would decrease since the stack would require less active area for a given output power. On top of that, some applications requiring high power densities can benefit from the use of materials permitting operation at higher current densities without flooding.

1.8 Scope of the work

The goal of the present work is to improve the complex liquid/gas transport in PEFCs. To do so, novel porous materials with patterned wettability have been developed. This development included the introduction of a new synthetic method based on radiation grafting, the extensive characterization of the modified porous materials and the final implementation of the optimized materials in fuel cell devices.

The radiation grafting method has been widely employed at the PSI Electrochemistry Laboratory for the preparation of low cost proton conducting membranes for PEFCs[13, 22]. The production of PEM is based on modification of thin flat (10-50 µm) polymeric films. In terms of chemical reactions, this work has focused on the translation of the radiation grafting method to thick porous (~200 µm) materials. Concerning the production of mask-assisted localized modifications, this work brings significant learnings on the use of electrons to modify porous substrates and discusses the influence of electron beam energy on the resolution through experiments and numerical
simulations. After successfully producing the GDLs with patterned wettability they have been tested using two main types of experiments: \textit{ex situ} measurements to characterize the capillary pressure characteristic and \textit{in situ} performance evaluation with simultaneous imaging to quantify the water distribution in operating cells.

The present thesis is built up as a combination of published (or submitted) peer-reviewed articles and some newly written chapters. The following lines will summarize the contents and structure of this PhD thesis. The first two chapters and Chapter 8 have been newly written. Chapter 1 introduced and motivated the research on optimized gas diffusion layers and provided the reader with the fundamental concepts that appear in the following chapters. Chapter 2 contains a collection of the experimental techniques, methods and details of numerical simulations used throughout this work. Chapter 3 describes the synthetic method in more detail and contains the initial proof-of-principle demonstrating the potential of these novel materials to improve fuel cell performance. Extensive synthetic details to translate from electron radiation grafting in flat systems to porous media are given in Chapter 4. It also includes \textit{ex situ} characterization of the chemical properties and how they correlate with material wettability. The chapter closes with a preliminary study on thermal degradation. Once a detailed understanding about grafting in porous media and wettability is provided, Chapter 5 focuses on the production of patterns using blocking masks. This chapter, of a more fundamental nature, presents a combination of experiments and Monte Carlo simulations on electron transport in solids and sheds light on the influence of electron energy in the pattern resolution. Later, Chapter 6 presents a thorough experimental study based on capillary pressure characterization of various modified materials. In this parametric study, the influence of different material properties (substrate, coating load, pattern design and chemistry) is elucidated by measuring water distribution with neutron radiography and X-ray tomographic microscopy. After the understanding of liquid water transport in modified GDLs, Chapter 7 focuses on \textit{in situ} characterization of PEFCs containing GDLs with patterned wettability. The impact of using microporous layers, and of different operating temperatures and relative humidities are studied, while water distribution is simultaneously imaged using neutron radiography. Finally, Chapter 8 contains conclusion and suggestions for future work.
Chapter 2. **Methods and experimental techniques**

This chapter presents the collection of experimental techniques and methods used in this PhD thesis. It starts by describing the substrate materials evaluated and the experimental procedures used to synthetize the modified samples. Further, the *ex situ* characterization techniques used to quantify chemical composition and wettability are presented, with a particular emphasis on imbibition dynamics. Later, the capillary pressure setup developed during this work and the *operando* testing station and diagnostics are described. Most of these experiments were performed with simultaneous neutron imaging of the cells. The image processing part is discussed in a follow-up subsection and the chapter closes by briefly presenting the numerical simulation work done in the frame of this dissertation.

Most of the information presented in this chapter can also found in the experimental sections of the respective following chapters. However, the objective of this chapter is to provide a compact collection of methodological descriptions that allows the reader to find the desired information efficiently.
2.1 Material synthesis

This section comprehensively describes the production of modified materials, mainly polymer films and GDLs, from the precursor plain substrates to the final cleaning procedure.

2.1.1 Substrate materials

While the final goal of this work is to produce GDLs with patterned wettability, other materials, such as polymer films and porous PTFE have been used as model substrates to evaluate the wettability changes on systems which are easier to understand. They are described in the following paragraphs.

2.1.1.1 Polymer films

Due to the complex nature of GDLs – heterogeneity and three-dimensional structure – the assessment of wettability and chemical composition is not straightforward. For that reason, flat polymer films were used as model systems representing the polymeric coating of GDLs. The flat nature of the system and its homogeneity makes the analysis much easier and fast characterization techniques can be applied to quantify the wettability and grafting yield. The following two polymers were tested:

- Polytetrafluoroethylene (PTFE) rolled foils (25 μm thick) were purchased from Ulraplast GmbH (Türkheim, Germany).
- Fluoroethylene propylene (FEP) rolled foils (25 μm thick) were purchased from DuPont® (TEFLON® FEP 100).

Samples of 16 cm x 14 cm were punched, rinsed with abundant ethanol to remove contaminants, dried under vacuum and packaged into zip-lock bags before irradiation. Some preliminary tests showed that the grafting kinetics (at a given monomer concentration, temperature and dose) were significantly faster using the FEP system. Moreover, the resistance to ionizing radiation of FEP is superior to that of PTFE\[78\], which becomes brittle at doses as low as 7.0 kGy (elongation at break drastically decreases). A better resistance is offered by FEP, with elongations at break around 200% after 12.0 kGy irradiation in air atmosphere.

Additionally to the aforementioned advantages, FEP is slightly more hydrophobic than PTFE and the sintering temperature is lower (~267°C for FEP and ~340°C for PTFE). For all these reasons, we have chosen FEP as the polymer for coating the GDLs and for performing parametric studies on flat films (Chapter 4).
2.1.1.2 *Gas diffusion layers*

Different types of GDLs have been used in this project. As a pivotal base material, we used Toray carbon paper due to its fairly narrow pore size distribution and the low fraction of carbon fiber coverage with binder. The initial idea was to have a rather uncovered substrate material in which the FEP coating could effectively cover fiber surfaces and be subsequently grafted – the presence of binder, like in SGL materials, complicates the analysis. Table 2.1 summarizes the GDL materials used in this thesis, alongside with their main properties:

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Grade</th>
<th>Type</th>
<th>Porosity [%]</th>
<th>Thickness [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toray</td>
<td>TGP-H-060</td>
<td>GDL</td>
<td>78</td>
<td>190</td>
</tr>
<tr>
<td>SGL</td>
<td>24 AA</td>
<td>GDL</td>
<td>88</td>
<td>190</td>
</tr>
<tr>
<td>Freudenberg</td>
<td>H2315</td>
<td>GDL</td>
<td>75</td>
<td>210</td>
</tr>
<tr>
<td>Gore</td>
<td>MP30Z</td>
<td>MPL</td>
<td>-</td>
<td>50</td>
</tr>
</tbody>
</table>

The studies reported in Chapter 4 and 5 were done using exclusively Toray TGP-H-060 coated in-house with FEP. The studies presented in Chapter 6 include a comparison of different types of GDLs (SGL, Toray and Freudenberg) and Chapter 7 is based on Toray materials with self-standing MPLs.

![Figure 2.1 – Scanning electron micrographs of different GDL cross-sections: SGL, Toray and Freudenberg. The resin method was used for the preparation of the cross-sections.](image)

The water transport in GDLs depends on the surface properties (i.e. wettability) and microstructure of the substrate. That is the reason why different types of GDLs have been used. Freudenberg materials have the narrowest pore size distribution and smaller average pore diameter, followed by Toray. SGL substrates present a bimodal pore size...
distribution (due to the presence of abundant binder) with a rather broad behavior. The cross-sections prepared with epoxy resin shown in Figure 2.1 illustrate this well.

2.1.1.3 *Porous PTFE*

In Section 2.3.4, the characterization of intrinsic (or internal) wettability will be discussed in the light of the Washburn theory. This method is based on measuring imbibition dynamics, i.e. the speed of liquid ascent inside a porous medium. In order to evaluate the adequacy of the method, we decided to use homogeneous porous materials with different pore sizes. Porous PTFE was obtained from POREX (Aachen, Germany). The different grades of “POREX® Microporous PTFE” and their main properties are listed in Table 2.2.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Pore size [µm]</th>
<th>Porosity [%]</th>
<th>Water intrusion pressure [mbar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM0510</td>
<td>4-7</td>
<td>40-45</td>
<td>410-690</td>
</tr>
<tr>
<td>PM1010</td>
<td>7-14</td>
<td>45-50</td>
<td>210-590</td>
</tr>
<tr>
<td>PM2010</td>
<td>15-25</td>
<td>50-60</td>
<td>140-350</td>
</tr>
<tr>
<td>PM5010</td>
<td>40-75</td>
<td>55-60</td>
<td>7-140</td>
</tr>
</tbody>
</table>

2.1.2 *Coating procedure*

2.1.2.1 *Dispersions used*

As already mentioned, FEP was the polymer of choice for coating the GDL. However, PTFE was also tested in our preliminary experiments. In both cases, water-based dispersions of polymer particles were used. These dispersions are composed of: solid polymer particles, a non-ionic stabilizer and solvent (composed of water, ethanol and some additives to adjust the pH, such as ammonium hydroxide). The following two dispersions were used in this project:

- Teflon™ PTFE DISP 30, purchased from DuPont®, has a solid content of 60%wt., a surfactant content of 6%wt. and an average particle diameter of 0.22 µm.
- Teflon™ FEPD 121, purchased from DuPont®, has a solid content of 55%wt., a surfactant content of 5.5%wt. and an average particle diameter of 0.18 µm.
2.1.2.2 Application of the coating

As shortly mentioned in Chapter 1, the coating was applied following the “dipping” method. The main steps of the method are:

1. The porous substrate was immersed into the dispersion, which can be used as received or diluted with water to the desired concentration. A certain time should be allowed for the complete impregnation of the dispersion. In this work, the samples were impregnated for 1 minute.
2. The impregnated substrate was brought to three different temperatures in order to: first, evaporate the solvent; second, evaporate the surfactant; and third, sinter the polymer. The programmed temperature profile and the actual measured temperature are shown in Figure 2.2. The first step could be done under atmospheric pressure or vacuum. Some groups reported that a more homogeneous distribution of the coating (through-plane) was obtained by using vacuum.\[79,81\]. However, we did not find a significant effect and therefore worked under atmospheric pressure.

![Figure 2.2 – Comparison between programmed temperature profile and measured values in two locations of the oven (\(T_{\text{oven,1}}\) and \(T_{\text{oven,2}}\)).](image)

2.1.3 Blocking masks

Blocking masks are needed to selectively stop the radiation and “guide” the electrons to activate the desired regions. The masks used in this work were manufactured by cutting the desired shapes out of stainless steel (316L) plates (Figure 2.3). Depending on the opening width requirements, two technologies were used for the mask manufacturing:

- Conventional waterjet cutting was performed at Waterjet AG (Aarwangen, Switzerland) and allowed for the preparation of rectangular slits of down to
250 μm width in 2 mm thick stainless steel. It is a cold cutting process in which pressurized water (up to 6 000 bar) is accelerated to a velocity of around 1 000 m·s⁻¹ to cut a variety of materials⁸².

- Laser micro-jet cutting was performed at Synova S.A. (Ecublens, Switzerland). This technique is based on a combination of water jet and a laser, where the water jet guides the laser by internal reflections⁸³. Using this technology, 100 μm wide slits were cut into 2 mm thick stainless steel, which was not possible with the previous technology. The manufacturing of 100 μm slits spaced by less than 1 mm was not possible in 2 mm thick steel due to thermal effects leading to material bending. When the mask thickness was reduced to 0.5 mm, this problem disappeared and narrower separation was possible.

![Figure 2.3](image-url)

**Figure 2.3** – Optical micrographs of two masks prepared with different procedures: (a) using a pressurized water jet; (b) using a combination of laser and water jet.

Several masks were manufactured in the frame of this project and were used for preparing materials with different pattern designs. The specific mask design and opening-spacing parameters will be described in the corresponding chapters.

### 2.1.4 Electron beam sources

Two different electron beams were used in this project. Apart from geometrical and structural details, they notably differ in the energy range. While extensive details can be found in Chapter 5, a brief description is provided here:
- **Medium-energy range:** an EBLab 200 sealed laboratory emitter system from Comet AG (Flamatt, Switzerland) was used at the Fachhochschule Nordwestschweiz (FHNW, Windisch, Switzerland) for these experiments. An acceleration voltage in the range of 80-200 keV (Chapter 5) was used. Samples and masks were placed on frame-like holders sealed by using a combination of polyethylenteraphtalate (PET) foil and an O-ring. This was done in order to minimize contamination from potential decomposition products. Samples were beamed under nitrogen (<200 ppm oxygen) with a conveyor speed of 12 m⋅min⁻¹ and a nominal air gap of 10 mm.

- **High-energy range:** a linear accelerator was used at LEONI Studer (Däniken, Switzerland) with a variable electron energy range of 1.05-2.35 MeV. The samples and masks were placed on top of metallic trays which convey the samples through the concrete shielded irradiation chamber.

Preliminary studies were performed in order to find the optimal dose. The experiments described in this thesis, if not otherwise stated, were carried out using a dose of 50 kGy. In both cases, polyethylene (PE) was placed between the samples and the holders to minimize backscattering (see Chapter 5 for more details).

### 2.1.5 Grafting reaction

The present subsection discusses the grafting polymerization reaction steps, the reactors used and also includes a collection of the chemicals employed for such a purpose.

#### 2.1.5.1 Preparation steps

The main steps can be summarized as:

1. Sample and monomer solution were placed in the reactor.
2. Nitrogen was bubbled through the solution during 60 minutes to remove the oxygen (8 NL⋅min⁻¹).
3. The reactor was sealed.
4. The reactor was placed in a temperature regulated bath (50-70°C) and the reaction started.
5. When reaction time was completed, the reactors were taken out from the baths and quickly cooled down and opened.
6. Samples were cleaned according to specific procedures (explained in 2.1.6).

This is the standard sequence we used when grafting on films and on GDLs with the NVF monomer. In case of grafting GDLs with AA, a special reactor providing vacuum was used to ensure that the monomer solution penetrates into the internal porosity.
2.1.5.2 Reactors

For a successful grafting reaction to take place, the chemical reactors need to provide the following functionalities:

- Having lines and distributors allowing for preliminary nitrogen bubbling in order to remove the oxygen.
- Being sealed and tight to avoid oxygen contamination during reaction.
- Provide efficient heat transport between reactor body material and monomer solution to equilibrate the temperature rapidly.
- Accommodate the given materials without risk of breaking.

![Photographs of the reactors used in this work: (a) basic glass reactor; (b) reinforced glass reactor; (c) cylindrical reactor under vacuum; (d) large steel reactor.](image)

**Figure 2.4** – Photographs of the reactors used in this work: (a) basic glass reactor; (b) reinforced glass reactor; (c) cylindrical reactor under vacuum; (d) large steel reactor.

In this context and depending on the sample type and size, various reactors were used (Figure 2.4):

- The standard reactor is typically used for the production of proton conducting membranes (shown in Figure 2.4.a). This reactor, made in glass and PTFE, has an approximate volume of 60 mL and was used for small foil samples (8 cm x 6 cm) and for small GDLs (5 cm x 1.5 cm) when vacuum is not needed.
- For the case of larger samples, when there was a need of being able to see the inside (for example, to check for the absence of bubbles), a larger glass reactor was used (Figure 2.4.b). This reactor was purchased from Büchi AG (Uster, Switzerland) and permits carrying out reactions in an absolute pressure range of 0-8 bar.
- When vacuum was required, as for the grafting of GDLs with an aqueous solution of acrylic acid, a dedicated reactor system was built using steel and glass parts (Figure 2.4.c). Extensive detail about the reaction design and operation are given in Chapter 4 (Section 4.3.7). The reactor has a volume of around 40 mL and GDL samples of 5 cm x 1.5 cm can be effectively grafted.
When much larger samples were needed, a rectangular, narrow steel reactor was used (Figure 2.4.d). It has a volume of around 600 mL and a sample size of 16 cm x 20 cm can be accommodated. Reinforcements were made in order to be able to operate the reactor under vacuum.

### 2.1.5.3 Monomers

Two monomers were extensively used for the present studies: acrylic acid (AA) and N-vinylformamide (NVF). AA (Sigma Aldrich) had a purity of 99% and contains 180-200 ppm of 4-Methoxyphenol (MEHQ) as inhibitor. The monomer was used as received and diluted in ultrapure water down to the desired concentration. NVF (Sigma Aldrich) had a purity of 98% and contained 22-55 ppm 4-hydroxy-TEMPO as stabilizer. NVF was used as received and diluted in ultrapure water when required. In preliminary experiments, NVF purchased from Tokio Chemical Industries and was tested as received and after distillation under vacuum to remove the stabilizer. While the purification process resulted in significantly improved grafting kinetics, the overall reaction rate was too low compared to that of the NVF acquired from Sigma Aldrich. For this reason, only NVF purchased at Sigma Aldrich was used. Chapter 4 contains a parametric study of grafting kinetics and effect of monomer concentrations for both AA and NVF monomers.

### 2.1.6 Cleaning procedure

The cleaning was found to be a key step for the production of high quality GDLs with patterned wettability. As shown in Figure 2.5, a vacuumed filter station was used to force the solvent to flow through the GDLs. This was done in order to promote a convective flow that could more effectively remove contaminants. When the sample was merely immersed in the solvents for several hours, the samples remained uncleaned, especially in the case of acrylic acid. In other words, the supposedly hydrophobic regions appear partially hydrophilic due to homopolymer (or unreacted monomer) still trapped in the material.

![Figure 2.5 – Illustration of the cleaning procedure using vacuum.](image-url)
A sequence of three solvents was used: ethanol, isopropanol and finally water. Approximately 300 mL of each solvent were used per sample. The solvents were re-used several times before disposal.

2.2 *Ex situ* characterization of physicochemical properties

This section describes the collection of analytical techniques used for the characterization of chemical composition and physical properties of the modified materials.

2.2.1 Gravimetric method

In the case where the mass increase due to the grafting polymerization reaction is sufficiently large, the gravimetric method can be used. It is simply based on measuring the difference in weight between the original polymer \( m_0 \) and the final copolymer \( m_F \), according to the following formula:

\[
DG \, (\%) = \frac{m_F - m_0}{m_0} \times 100
\]  

(2.1)

This method was successfully applied to polymer films, but not to GDLs. The change in weight on modified GDLs was too low to provide \( DG \) values with a sufficient accuracy.

2.2.2 Infrared spectroscopy

In order to obtain information about the chemical bonds present in the modified samples and to compare the composition through the bulk and at the surface of the material, *Fourier transform infrared spectroscopy* (FTIR) was performed in both transmission and *attenuated total reflection* (ATR) modes (Figure 2.6). The FTIR measurements were exclusively performed on polymer films.

A Vertex 70v FTIR spectrophotometer (Bruker) was used. Spectra were acquired under vacuum at 4 cm\(^{-1}\) resolution between 400 and 4000 cm\(^{-1}\). A horizontal ATR accessory - ZnSe crystal at 45° angle of incidence- was used for the complementary measurements. The OPUS software was used for baseline subtraction. Extensive details of the peak identification, integration, normalization procedure and final quantification can be found in Chapter 4.
2.2.3 X-ray photoelectron spectroscopy (XPS)

Since FTIR could not be performed on modified GDLs due to the excessive absorption of the substrates, another method was chosen for measuring the bond vibration signals on the GDL coating. XPS was performed on baseline and modified GDLs with both AA and NVF systems, and allowed successfully identifying the expected bonds due to grafting onto the coating.

XPS measurements were carried out with a VG ESCALAB 200iXL spectrometer (Thermo Fischer Scientific) using monochromatic AlKα X-ray radiation (1486.6 eV) with a beam size of ~500 μm², which we assume is large enough to provide reliable average information. The spectrometer was calibrated using the Ag 3d₅/₂ peak at the binding energy (BE) 368.3 eV. The pressure in the analysis chamber was about 2x10⁻⁹ mbar abs. The spectra were recorded in constant analyzer energy mode at a pass energy of 30 eV. The BE normalization was done based on the C-C (GDL) peak at 284.5 eV.

2.2.4 Energy dispersive X-ray spectroscopy (EDX)

EDX was used to quantify the elemental composition of baseline materials and modified GDLs. A compatible accessory (EDX TSL, AMETEK) was implemented into a scanning electron FE-SEM Ultra 55 microscope (Carl Zeiss, Oberkochen, Germany). If otherwise not stated, a voltage of 8 keV, an aperture of 60 μm and a gun-to-sample distance of ~9 mm were used. EDX was used mainly in two modalities: to obtain average elemental composition of a given sample spot (Chapter 4) or to obtain elemental mappings (Chapters 3, 5 and 6). With regard to the latter, it was applied to the study of two different distributions benefiting from the acquisition of local chemical
information: the hydrophilic patterns onto GDL surfaces and the FEP coating distribution over the through-plane direction.

2.2.4.1 Elemental mappings: hydrophilic patterns

Extensive work has been performed in the frame of this PhD thesis to obtain quantitative information out of elemental EDX mappings for the characterization of the hydrophilic patterns. We systematically tested various parameters for map acquisition, such as electron energy, resolution and number of frames. While more information on image processing and extraction of quantitative data is provided in the following chapters (in particular in Chapter 5), we concluded that the selection of 512 x 400 px and 64 frames for obtaining the mappings was a good trade-off between acquisition time (≈51 min) and image quality.

2.2.4.2 Elemental mappings: coating distribution

The basic idea of this measurement is to identify coating locations by mapping the fluorine signal (which is only present in the hydrophobic coating). We did so in order to find a valid coating procedure (thermal treatments) that provides well-distributed coating and notably-covered carbon fibers. An example of these mappings can be found in Chapter 3 (Section 3.3). Due to the mechanical properties of the GDL and the presence of numerous fibers oriented in different directions, the preparation of clean cross-sections was a challenging task.

![SEM micrographs of GDLs cross-sections prepared using different techniques](image)

Figure 2.7 – SEM micrographs of GDLs cross-sections prepared using different techniques: (a) manual cutting using knife; (b) ion beam gun; (c) cryo-microtome; (d) epoxy resin impregnation and mechanical polishing.
We tested different techniques, as shown in Figure 2.7, and concluded that the resin impregnation method followed by polishing with small size grain led to the best results in terms of accurate identification of coating locations; however longer preparation times were required. This is also the case for cross sections prepared using cryomicrotome. The use of ion beams provided smooth surfaces but seems to be an invasive technique. In other words, the atoms removed by the beam may relocate to different positions leading to a totally different structure. For qualitative results and fast comparison, manual cutting with a knife of previously frozen GDLs (with liquid nitrogen) can be used, but quantitative results are challenging to obtain and depend notably on the quality of the cut.

2.3 Characterization of wetting properties

During this PhD work, a particular focus was put on understanding and quantifying wettability. For that reason, we dedicate a complete section to the various characterization techniques that have been used and adapted for this purpose.

2.3.1 Static contact angle

When a liquid droplet is placed on top of a substrate – the so called *sessile drop measurement* –, there are two possibilities: (1) the droplet quickly finds a static shape and stays on the surface or (2) in the case of a porous substrate, the droplet can be wicked (totally or partially) by the solid. It is assumed that, in the time frame of these events, evaporation is negligible, which is a realistic approximation if the droplet is not too small and volatile liquids such as hexane are avoided.

![Figure 2.8 - Examples of static contact angle measurements (hydrophilic and hydrophobic) on flat films and porous GDLs.](image)

Figure 2.8 – Examples of static contact angle measurements (hydrophilic and hydrophobic) on flat films and porous GDLs.
As described in the previous chapter (Figure 1.4.3), if a non-porous, flat surface is used, the interpretation of wettability and contact angle is straightforward. In this work, static contact angles were measured for flat films and for GDLs. In the case of GDLs, the observed contact angle is a characteristic affected by both the surface properties (intrinsic contact angle) and the material microstructure, and the result of the sessile drop measurement is referred to as “apparent contact angle” (Chapter 4).

An in-house built contact angle goniometer was used for these measurements (Figure 2.8). It essentially consists of a flat movable surface to hold the sample, controllable light, volumetric equipment to accurately place the droplets and a camera (Conrad Digitale Mikroskopkamera USB 9 Mio. Pixel). The droplet volume was 2 μL is every case and, at least, 5 droplets were measured per sample. The extraction of the contact angles (on both sides) was performed using the ImageJ software.

### 2.3.2 Sorption dynamics

When GDLs were treated under certain conditions rendering them highly hydrophilic, the solid spontaneously wicks the liquid and the final state does not allow distinguishing the characteristics of different samples. In this case, the sorption dynamics (see Figure 2.9) were used as an additional characterization method.

For this purpose we used a commercial goniometer (OCA 25 Dataphysics) equipped with a CCD camera with higher framerate (34.5 fps). Again, a droplet volume of 2 μL was used in every case and different GDLs were compared under the same conditions. At least 4 repetitions per sample were taken. The image processing was done with a commercial software (SCA 20, Dataphysics) using ellipsoidal fitting to extract valuable droplet parameters (contact angle, volume, height, etc).

\[ t = 0 = t_0 \quad t > 0 \quad t = t_f \]

![Figure 2.9 – Illustration of a droplet being wicked by a porous substrate](image)

In this particular work, we used the droplet volume, \( V(t) \), as a parameter to calculate the absorbed volume over time. More details are given in Chapter 4.
2.3.3 **Internal contact angle: the Washburn method**

2.3.3.1 *Fundamentals*

As discussed in the previous chapter, the internal contact angle is the variable impacting capillary pressure and consequently water transport. For that reason it is important to obtain information about the wettability of internal pore walls. One possible method is based on measuring the liquid imbibition dynamics, which depend on both pore size and internal contact angle, with the so called Washburn method. The parameters are obtained by fitting model variables to the experimental data. Two approaches are possible: either a measurement of the mass gain\(^8\) (experimentally more complex) or the height over time\(^\text{9}\). The internal wettability in GDLs can be seen as a complex phenomenon due to the presence of several media (carbon fibers, coating and binder); however, the use of a statistical average internal contact angle has been proposed\(^\text{8}\).

A complete energy balance\(^\text{8}\) was considered and terms related to inertia and frictions were found to be negligible. Therefore, the capillary pressure term equals the sum of the viscous forces and the gravitational effects:

\[
\frac{dh}{dt} = \frac{R_P^2}{8 \mu h} \left( \frac{2 \gamma_{lv} \cos \theta_{int}}{R_P} - \rho gh \right) \tag{2.2}
\]

where \(h(t)\) is the height of the liquid filled region, \(\rho\) is the density, \(\mu\) is the dynamic viscosity, \(\gamma_{lv}\) is the surface tension of the liquid-vapor interface, and \(R_P\) is a parameter describing an average pore size. The method is easily applicable to hydrophilic samples where the water rises, yet it presents practical limitations when hydrophobic materials (like usual GDLs) are tested. To solve this issue, the Owens-Wendt method can be implemented. This method is based use of different solvents with lower surface tension that spontaneously imbibe the substrate to the extrapolate the value of internal contact angle for water\(^\text{8}\).

2.3.3.2 *Experimental setup and image processing*

A schematic of the setup built for the characterization of imbibition dynamics is shown in Figure 2.10. Five samples were sandwiched between two Plexiglas plates covered with magnetic tape. A parallel arrangement of the samples was assured by using a positioning tool. After that, the samples holder was introduced into the glass container which was closed with an aluminum lid and sealed with a paraffin film. A thermocouple and the needle of the syringe for liquid injection were passing through drilled holes into the chamber. Approximately 15 mL of the solvent were initially delivered to the system to allow for saturation of the vapor phase with the solvent (evaporation from the GDL can
be an important issue). A time of 20 min was found to be enough to saturate the chamber. The solvent was pumped in with a syringe pump (BS-300, Braintree Scientific Inc.) at a rate of 6.0 mL/min and a video was recorded at 15 frames/s (DigiMicro Profi 200.5) and 512 x 468 px. The camera was elevated with respect to the interface plane between sample and solvent (defining a certain angle) in order to avoid the disturbance brought about by the meniscus established between glass container and solvent. After the identification of the inhibition point (clearly visible by the formation of a meniscus GDL-solvent) the pump was stopped.

**Figure 2.10** - Schematic of the Washburn setup and its components: (1) Programmable syringe pump; (2) Samples container; (3) Samples holder; (4) Digital Microscope Camera; (5) White light; (6) Computer for data acquisition.

The image processing (Figure 2.11) was performed as follows: first, each image was converted to grayscale and divided by an average “dry background” image corresponding to the average of 20 images before the start of imbibition, in order to improve the contrast between dry and saturated GDL. Then the solvent height in pixels was extracted automatically for each image and each sample using an in-house software written as an ImageJ plugin. Finally, the pixel size was converted to a height in cm taking into account the effect of the camera angle.
Figure 2.11 – Original images “as recorded” before imbibition starts (a) and after 5.67 seconds (b). Normalized images before imbibition starts (c) and after 5.67 seconds (d).

2.3.3.3 Selection of results

A detailed presentation of results and learnings obtained with the Washburn method is not meant to be given here. However, a summary of the most representative results is provided. Initially, we compared imbibition dynamics of four different grades of porous PTFE. In this case, the internal contact angle can be assumed to be the same for every case since the material is purely composed of PTFE. That being said, the microstructure is the only parameter that varies between samples, in particular the average pore diameter. The observed trends (Figure 2.12.a) are as expected: smaller pores lead to slower liquid rising rate.

Figure 2.12 – Washburn curves for porous PTFE substrates with increasing average pore diameter. (a) Plain materials; (b) grafted PTFE substrates. Hexane was the liquid used.
The very same materials measured in Figure 2.12.a were then grafted with acrylic acid (PTFE-g-pAA) and significantly faster imbibition dynamics were obtained, as logically expected (Figure 2.12.b). In this case, the contact angle has been decreased thanks to the formation of a hydrophilic copolymer. If the microstructure would remain exactly the same (i.e. very thin grafting only leading to modifications in the nm range), then the changes in the curves would only be due to the variation in internal wettability. This is however very unlikely since we could visually identify notable structural variations in the modified porous PTFE.

The case of a real GDL material is much more complicated due to the presence of different surfaces (carbon, coating and, for some samples, binder). We present here the case of a Toray TGP-H-060 coated with 70%wt. FEP and subsequently grafted with NVF, analyzed using hexane and water. Hexane was used for characterization purposes since it can be assumed that the solvent fully wets (contact angle of 0°) the surfaces of the GDL due to its low surface tension. The value of contact angle being known, the other parameter (pore size) can be extracted. Afterwards, imbibition dynamics were measured using water as liquid (Figure 2.13) and, using the \( R_P \) extracted from the previous experiment, the intrinsic contact angle was calculated. In this case a value of 76° was obtained. It is worth mentioning that this obtained value is probably underestimated. One of the method’s flaws is to assume that the effective \( R_P \) is the same for both liquids. In the case of water, there is probably a fraction of the pore walls which remains uncovered, resulting in a lower dynamics and thus a higher contact angle.

![Figure 2.13 - Washburn curves of Toray 70% FEP grafted with N-vynilformamide, measured with hexane and water (dots) and the corresponding fitted theoretical Washburn curves (lines).](image)
2.3.3.4 Conclusions

In conclusion, the Washburn method presents several limitations to obtain quantitative results for hydrophobic GDLs which restricted its utilization. Although a more detailed explanation can be found in our previous work\[89\], the main limitations were identified when the fitting of model parameters to experimental data led to no solution (\(\cos \theta_{\text{int}} > 1\)) for some materials (uncoated GDLs when hexane was chosen as reference), using ethanol and acetone as a liquid. This is contradictory with previous literature\[84, 87, 90\] which reported \(\cos \theta_{\text{int}} < 1\) in every case when measuring with these liquids. Different reasons could contribute to these differences:

- The experimental error implicit in the measurements could explain that, since there is a high sensibility of the parameter \(R_p\).

- Both parameters \(R_p\) and \(\cos \theta_{\text{int}}\) compensate each other, therefore the iterative calculation has not a unique solution. Some groups fitted the equation by iterating both parameters, however nothing was said about the values of \(R_p\); others\[90\] estimated the \(R_p\) (or Washburn constant) and then only resolve for the contact angle (this work’s approach).

- The assumption that the complex pore structure of the GDL is equivalent to a parallel capillary tube and that the liquid pore volume is saturated may be not accurate enough. The parameter \(R_p\) is not assumed to be consistent with the real pore radius, but rather the hydraulic radius\[91\]. Depending on the liquid’s surface tension, viscosity and density, a liquid could rise up in pores that are not accessible for other liquids.

- The concept of “statistical average contact angle” should be handled with care. Possibly the liquid wets only (or preferentially) the GDL component with the higher surface tension which better interacts chemically with the solvent.

That being said, the Washburn method provides a fast and valuable semi-quantitative characterization technique for hydrophilic samples, which spontaneously imbibe liquid water.
2.4 Characterization based on saturation vs. capillary pressure

A section of Chapter 3 and the complete Chapter 6 will focus on \textit{ex situ} characterization of modified GDLs based on their \textit{saturation} versus \textit{capillary pressure} characteristic. A setup was specifically built for this purpose, which will be extensively described in Chapter 6. A few remarks are provided in the following paragraphs.

2.4.1 Fundamentals

As described in the previous chapter, the gradient in capillary pressure is one of the main driving forces for liquid water transport in PEFCs. It is therefore relevant to measure the capillary pressure characteristic of different materials using an \textit{ex situ} experiment for two reasons: (1) to find candidates among modified materials to be tested in operando cells; and (2) to fundamentally understand the influence that various material parameters have on the liquid water capillary transport. The method we have chosen to characterize the GDLs is based in the \textit{Method of Standard Porosimetry} (MSP)\cite{92} which was initially adapted to GDLs by Gostick et al.\cite{93}.

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{figure2.14.png}
  \caption{Simplified sketches showing the main components of a capillary pressure characterization test rig. (a) The traditional test rig; (b) setup developed in this PhD thesis.}
\end{figure}

The general idea is depicted in Figure 2.14. In the traditional test rig, the water is injected uniformly from the bottom interface through a hydrophilic membrane placed underneath the porous material of interest (GDL in this case). When the pressure of the liquid, $P_L$, is increased the open space of the porous material increasingly fills with water. When an interconnected network of pores spanning the thickness of the material is filled with water, it is said that breakthrough occurs. The capillary pressure, $P_C$, at which this occurs, is referred to as \textit{breakthrough capillary pressure} in the GDL literature. In an operando cell, once this point is reached, water should preferentially flow through this “low-resistance” pathways. In the MSP, however, a hydrophobic membrane (with
small pores) is placed on top of the porous material thereby setting a very high capillary pressure barrier for the water to go through. In consequence, the liquid is forced to completely saturate the sample before actually being able to penetrate the pores of the hydrophobic membrane. This guarantees complete saturation.

The pressure of the gas, $P_G$, is monitored at any time and the capillary pressure is calculated as:

$$P_C = P_G - P_L$$  \hspace{1cm} (2.3)

At a given $P_C$ the saturation needs to be assessed. Many approaches reported in the literature rely on the measurement of weight change to calculate saturation as the difference between dry and wet sample. In our case, we did simultaneous imaging (neutron radiography or synchrotron X-ray tomographic microscopy) to quantify the saturation locally. Since we are especially interested in how the water redistributes on the porous material, imaging methods are required in this case. The liquid saturation, $s_L$, can be calculated as:

$$s_L = \frac{V_L}{V_{void}} = \frac{t_L}{t_{void}}$$  \hspace{1cm} (2.4)

where $V_L$ is the volume of liquid in the pores, $V_{void}$ is the volume of void generally filled with air or a mixture of air and vapor, $t_L$ is the thickness of liquid and $t_{void}$ is the thickness of void, calculated as:

$$t_{void} = \frac{V_{tot}}{A}\varepsilon$$  \hspace{1cm} (2.5)

where $V_{tot}$ is the total GDL volume for a given area, $A$, of material and $\varepsilon$ is the porosity defined as:

$$\varepsilon = \frac{V_{void}}{V_{tot}}$$  \hspace{1cm} (2.6)

The representation of saturation versus capillary pressure results in the so-called capillary pressure or $s_L$-vs-$P_C$ curves. While traditional measurements reported characteristics of homogeneously treated materials and therefore extracted average information over the complete sample area, we systematically differentiated the hydrophilic and hydrophobic regions in our analysis as two separate domains inside the same material. An example of this approach is presented in Figure 2.15.
Methods and experimental techniques

2.4.2 The setups

Two different setups have been used to obtain $s_L$-vs-$P_C$ curves. The main part of the setup is schematically shown in Figure 2.14. The two setups differ as follows:

- The homogeneous injection setup was developed by Lamibrac et al.\cite{26} and includes the use of a hydrophilic membrane and liquid distributors to ensure that water is homogeneously injected through the complete bottom interface. The circular sample size is around 6 mm in diameter. In this case, X-ray tomographic microscopy was performed at the TOMCAT beam line\cite{94} of the Paul Scherrer Institut during the experiment for selected capillary pressure points. In this case, since 3D information is obtained, the quantification of water saturation was performed by measuring the volume of liquid with respect to the void volume, based on segmentation. An illustration of the setup is given in Figure 2.16 and more details can be found in Chapter 6 and the following references\cite{26,95-97}.

Figure 2.15 – Capillary pressure curves differentiating between hydrophilic and hydrophobic domains.
The mono-channel injection setup has been specifically developed for this project (Figure 2.14.b). The hydrophilic membrane is not used in this configuration and water is injected through a central channel (1 mm width). The sample area is 10 mm x 10 mm. The reason to use a narrow channel in the center is two-fold: on the one hand side, important information about lateral transport (i.e. in-plane) is obtained and, on the other hand, a superimposed water layer coming from injection points and and the hydrophilic membrane is eliminated, allowing the use of 2D transmission imaging. Further details about the setup can be found in Chapter 6. The setup was built in aluminum and neutron imaging was performed at the ICON beamline\cite{98} of the Paul Scherrer Institut during the complete duration of the experiment to quantify the local saturation. Since radiographs were obtained, 2D water thickness is the information at hand. Using equation 2.4 the liquid saturation was obtained.

A further difference between the two setups is related to the way that the liquid pressure is controlled. While in the former it was controlled by injecting with a syringe pump, in the latter a water tank was lifted using a motorized platform and thus the height of the liquid column defines the pressure.
2.5 \textit{In situ} characterization

The ultimate goal of developing gas a diffusion layer with patterned wettability is, obviously, improving fuel cell performance. In particular, we would expect that bulk mass transport losses are reduced by a more efficient water management. Many modified GDLs were tested in operando cells using the “multicell” setup developed in the frame of the PhD thesis of P. Oberholzer\cite{Oberholzer15, Oberholzer29}, as described in the following subsections.

2.5.1 \textbf{Cell construction}

Differential cells were used for all \textit{in situ} measurements reported in this thesis (Figure 2.17). These are small cells operated under high gas flow to mimic local conditions of a larger technical cell. The use of differential cells allows removing of the inhomogeneity related to the change of conditions (gas composition, humidity) along the channel, and permits performing a more fundamental material comparison. In this particular work, we kept all other materials and assembly procedures the very same and only the cathodic GDL was varied to accurately study the effect of patterned wettability on fuel cell performance.

The cells were machined in aluminum and coated with a protective layer (25 \textmu m Ni, 10 \textmu m Au). They have 1 cm$^2$ of active area and the flow field is composed of five parallel channels (1 mm width, 0.55 mm depth) separated by 1 mm lands. Commercial catalyst coated membranes (CCMs) were purchased from WL Gore & Associates Inc. (Primea 5710), having catalyst layers with platinum loadings of 0.1 mgPt$\cdot$cm$^{-2}$ and 0.4 mgPt$\cdot$cm$^{-2}$ on the anode and cathode, respectively. The GDLs used in the anode were Toray TGP-H-060 coated with 30\%wt. FEP. When referring to cathodic baselines, the same material was used. In every other case, these GDLs were replaced by a modified baseline including patterned wettability, or another substrate. PTFE gaskets of variable thickness were used in combination with steel spacers to accurately control the MEA compression and ensure the gas tightness. When explicitly stated (Chapter 7), self-standing MPLs were added to both anode and cathode.
2.5.2 Multicell setup and test bench

The individual cells were assembled separately and used in the multicell setup, which permits simultaneous operation of six cells. Further details can be found in the original work in which this setup was developed\textsuperscript{[15, 99]}. The main advantages and particularities of this setup and test bench are as follows:

- The same humidified gas stream is fed to all cells, which improves reproducibility. With recent developments in cell assembly and components
developed in the frame of the PhD thesis of J. Biesdorf, a cell-to-cell reproducibility of ~20 mV was reported.[180]

- The flow rate for each individual cell is controlled by gas flow controllers placed downstream. This ensures a proper flow distribution between the cells.
- An advanced thermal control system based on actuators at three levels ensures that cell temperature of anode and cathode are accurately controlled for each cell.
- Material comparison is highly reliable and can be performed rapidly with this setup. For example, the effect of 3 different cathodic GDLs or 3 different membranes can be evaluated by building 3 pairs of cells.
- As beam time for performing neutron radiography measurements is limited, the simultaneous imaging of 6 cells represents a notable advantage. Additionally, the setup is specially designed to easily rotate the setup by 90° to switch between through-plane and in-plane modes, or vice versa. On top of that, the housing containing 6 cells can be easily and quickly replaced by a new housing without any modification in piping or test bench, thereby maximizing data generation productivity during neutron imaging campaigns.

In this particular work, the anodic flow rate was set to 0.4 NL·min⁻¹ and the cathodic to 1.0 NL·min⁻¹, corresponding to stoichiometries of >60 at 1 A·cm⁻² (differential condition operation). Pure hydrogen and air were used as reactants. Cells were operated at 50°C or 70°C, depending on the experiment. Generally, relative humidity (RH) of the anode gas was set to 100% and cathode RH was varied as described in the corresponding chapters. The test bench also offers the possibility of performing advanced diagnostics by switching between different gases. This is described in the following subsection.

Each individual cell contains printed circuit boards enabling a compact interface to assess measurements of voltage, current and temperature. The multicell setup can be operated in galvanostatic mode (cells connected in series and current is controlled) or in potentiostatic mode (cells connected in parallel and voltage is controlled). In all experiments herein reported, galvanostatic mode was selected. The membrane resistance was obtained by superimposing an AC current (5 kHz) to the constant cell current and measuring the voltage response. Afterwards, the high frequency area resistance (HFR) is calculated based on a Fourier transform of the voltage response at the corresponding frequency.
2.5.3 Pulsed gas analysis (PGA) method

In order to access different indicators of mass transport losses, the PGA method was used. The particularities of the method have been described in detail by Boillat et al. and will not be given here. In short, the fuel cells are operated under air and short pulses (1 s) of different gases are fed to the cathode side of the cell. These gases are helox (a mixture of helium and oxygen at the same ratio as nitrogen and oxygen in air) and pure oxygen. At a given time, the voltage obtained under helox, $U_{helox}$, and the voltage obtained under oxygen, $U_{O2}$, are recorded and the following information can be extracted:

1. By calculating the difference between the voltage under air and helox, an indicator of the bulk mass transport losses, $\eta_{bulk}$, is obtained, as:

$$
\eta_{bulk} = U_{helox} - U_{cell} \tag{2.7}
$$

where $U_{cell}$ is the cell voltage operated under air. This is so because the binary diffusion coefficient of oxygen in helium is a factor of ~3 larger than in nitrogen, due to a reduced molecular size.

2. By calculating the difference between the voltage under oxygen and helox and considering the charge transfer decreased overpotential due to a change in $c_{O2,ref}$, an indicator for the non-bulk mass transport losses is obtained:

$$
\eta_{non-bulk} \cong U_{O2} - U_{helox} - 0.045 \text{ V} \tag{2.8}
$$

where the 45 mV account for the increased thermodynamics and kinetics due to using pure oxygen. Both the Knudsen diffusion and thin film diffusion contribute to the non-
bulk losses. In this particular work, we target a reduction in the bulk losses and expect no significant effects on the non-bulk losses. However, since use of novel GDLs with patterned wettability leads to a notably different water distribution in the operating cells, all contributors to the mass transport resistance will be carefully evaluated (Chapter 7).

2.6 Imaging

The capillary pressure characterization and part of the in situ measurements were carried out while simultaneous neutron radiographs were taken. A selected experiment was imaged using synchrotron X-ray tomographic microscopy. It should be mentioned that the work carried out in the frame of this thesis did not aim an improvement in the imaging techniques, but rather the use of the state-of-the-art techniques readily available at the Paul Scherrer Institute. They are briefly described in this section.

2.6.1 Neutron radiography

Neutron imaging has been extensively used for imaging liquid water in PEFCs. The results presented in this thesis have been obtained from measurements performed at the ICON beam line of the SINQ spallation source at the Paul Scherrer Institut [98].

2.6.1.1 Through-plane

Through plane imaging corresponds to the configuration where the neutron beam is perpendicular to the membrane plane. Two different setups, one for the capillary pressure experiment (individual cell) and one for the in situ measurements (6 simultaneous cells) were used in this configuration. Some details are provided here to show the main differences between the two setups:

- For the capillary pressure measurements, a 20 µm thick Gd₂O₂S scintillator screen mounted on the micro-setup detector including a CCD camera (Andor DV436, 2048 x 2048 pixels) was used. The detector pixel pitch was 13.5 µm and the effective resolution 55 µm. The exposure time was set to 30 s and the readout time was 4 s. Chapter 6 contains further details.

- For the in situ imaging, a conventional neutron imaging setup was built with a neutron sensitive scintillator screen (⁶LiF/ZnS, 50 µm thick) perpendicular to the beam axis. A cooled CCD camera (andor iKon-L, 2048 x 2048 pixels) combined with optical lenses (Zeiss Makro-Planar, 100 mm focal length) was used. The resulting pixel size was 62.5 µm and the effective resolution 115 µm. Chapter 7 contains further details.
2.6.1.2 In-Plane

In-plane radiographs were only recorded for operando cells. In this case, anisotropic neutron imaging was performed. This is needed in order to obtain high resolution imaging in the direction of the different layers. The tilted setup was first reported by Boillat et al. and further details can be found in the original work[102]. In this particular work, a Gd$_2$O$_2$S scintillator (10 μm thick) was positioned behind the cell at an angle of 5.8° with respect to the beam axis, resulting in a magnification factor of ~10 in the horizontal direction. The pixel size was 6.2 μm and 61 μm in the horizontal and vertical directions, respectively. Effective resolutions of 12 μm and 140 μm were obtained using a horizontal L/D ratio of 1000 and a vertical L/D ratio of 100. The factor L/D = 1000 means that the beam divergence angle is 1/1000 rad. Chapter 7 contains further details.

2.6.1.3 Image processing

The image processing steps carried out in this project are very similar as in previous works of our group[24, 99, 103]. For that reason, only a brief description is provided here. The quantification of water content is based on the acquisition of images of cells under operation (and therefore with water) and dry cells (Figure 2.17). The image processing consisted of a correction of the detector background, filtering, a flat field correction, a correction of the background due to neutrons scattered by the setup and a correction of beam intensity fluctuations and cell displacements. Extensive details about these processing steps can be found in the PhD thesis of P. Boillat[103].

\[
\text{Relative transmission (}\frac{I}{I_0}\text{)} = \frac{\text{Cell with water}}{\text{Dry cell}}
\]

**Figure 2.19** – Schematics showing the general image processing protocol.

In the final step, the images were divided pixel-wise to the radiograms in the dry state. The thickness of water, $\delta$, was then calculated using the Lambert-Beer law:
\[
\frac{I}{I_0} = e^{-\Sigma \delta}
\]  

(2.9)

Where \(I\) is the intensity of the image with water, \(I_0\) is the intensity of the dry image, and \(\Sigma\) is the macroscopic cross-section of water which varies with the setup used\[104].

### 2.6.2 X-ray tomographic microscopy (XTM)

XTM was performed in combination with the capillary pressure setup shown in Figure 2.16. Similar to neutron imaging, no methodological change was done in the frame of this thesis and we used the previously developed high resolution XTM setup and image processing, as reported by Eller and Lamibrac\[26, 95-97]. The XTM was performed at the TOMCAT beamline of the Swiss Light Source (SLS) at the Paul Scherrer Institut. The beam energy was 13.5 keV and tomographic scans with 2001 exposures of 10 ms each were performed, resulting in a complete scanning time of 20 s. A PCO edge camera and 2-4 x zoom microscope were used to acquire the images, resulting in a pixel/voxel size of 2.2 \(\mu\)m. More details about image processing, segmentation and data quantification can be found in the original publication of Lamibrac et al.\[26]. While XTM radiographs at different GDL slices are shown in Chapter 6, surface renderings are shown in Figure 2.20 comparing the imbibition behavior of a commercial GDL with that of a modified sample, clearly showing the preferential accumulation of water in the hydrophilic domains at lower capillary pressure.

![Figure 2.20](image.png)  

**Figure 2.20** – XTM surface renderings of water imbibition into Toray TGP-H 060 gas diffusion layers; left: standard material (capillary pressure 30 mbar); right: modified material (capillary pressure 5 mbar).


2.7 Simulations

2.7.1 Electron transport in solids

Chapter 5 focuses on the formation of patterns with electron radiation grafting in porous GDLs. In particular, the influence of electron energy on the lateral resolution and dose distribution is studied by a combination of experiments and numerical simulations. The latter were carried out using an already existing code system, PENELOPE.

PENELOPE stands for “PENetration and Energy LOss of Positrons and Electrons” and it is a general purpose Monte Carlo code system for the simulation of coupled electron-photon transport in different materials. The code is distributed by the OECD Nuclear Energy Agency and uses state-of-the-art physics models \[105-107\]. The trajectories of electron showers impacting different materials can be simulated, as shown in a simplified example of Figure 2.21.

![Figure 2.21](image)

Figure 2.21 – Example of electron trajectories simulated using PENELOPE on 60 µm thick amorphous carbon for different electron energies.

Using the physics from PENELOPE, coded as a set of FORTRAN subroutines, we prepared a two scripts to: (1) define certain geometries to reproduce our experimental configurations; (2) a main script where the electron source geometry and parameters are introduced, the material bodies are set, the meshing is defined and the desired output parameters (dose or energy distribution) are specified.

In this particular work, the solid bodies were defined as prisms which are infinite in two directions \(x\) and \(y\), following the nomenclature of Chapter 5) and finite in direction \(z\). The electron source was defined as a prism which emits electrons of a given energy \(E\) mono-directionally (i.e. 180° with respect to the source). In most cases, \(10^7\) electrons were used for the simulations, providing a good trade-off between computational time and quality of results.
Chapter 3. Engineered water highways – a proof of concept

In this chapter the synthesis method based on electron radiation grafting is illustrated and compared with previously reported technologies to improve water management in gas diffusion layers. The presence of N-vinylformamide molecules in the hydrophilic regions is demonstrated with elemental mapping and correlated with the water distribution using a capillary pressure ex situ experiment imaged with neutrons. Finally, in situ characterization was performed and clearly showed that, by using the modified GDLs with patterned wettability, the fuel cell performance is improved at high current densities. This chapter should be taken as a proof of concept and shows the potential that these materials have to improve water management in PEFCs.

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### 3.1 Introduction and results

Polymer electrolyte fuel cells (PEFCs) have become a promising candidate for replacing fossil fuel fed engines in both stationary and mobile power sources, owing to their zero-emission characteristics, high efficiency and power density. Years of intensive research (from around 800 publications in 2000 to about 3000 in 2014, patents from 500 in 2000 to nearly 3000 in 2012)\textsuperscript{[108]} brought the technology to a status where commercialization appears realistic, with first systems recently appearing on the market for both stationary and mobile applications\textsuperscript{[109]}, specifically the latter at elevated price (47 $/KW\textsubscript{system} in 2012, 30 $/KW\textsubscript{system} being the target for 2017)\textsuperscript{[110]}.

Nevertheless, some technical issues remain, which require special attention, such as cost and durability, in which an important role is played by water management. The water management is not a trivial issue in PEFCs and needs to be carefully controlled. On the one hand, the membrane needs to be sufficiently hydrated to ensure practical proton conductivity (~0.1 S/cm). On the other hand, excessive amounts of water in the gas diffusion layer and flow field channels can hamper the access of reactant gases to the catalyst layer, leading to increased mass transport losses\textsuperscript{[111]}. Consequently, power density is reduced if the delicate balance between these two requirements is not fulfilled, resulting in an increased stack size – and cost – for a specified output power. Furthermore, some degradation mechanisms (e.g. starvation) are thought to be related to water flooding\textsuperscript{[112]}.

State of the art PEFCs include a gas diffusion layer (GDL), a porous layer made of carbon fibers responsible not only for the fine distribution of reactant gases, but also for the transport of product water, heat and electrical current. These functions imply a triple set of contradictory requirements: high diffusivity of the gas phase, high permeability of the water phase and high thermal and electrical conductivity of the solid phase. On the cathode, liquid water flows from the catalyst layer towards the gas flow channels through the GDL, in opposite direction to oxygen diffusion. Capillary pressure is the driving force for water transport\textsuperscript{[28]}, which depends both on the pore size and the internal contact angle between water and the porous medium, showing the importance of the microstructure and the surface energy of the material at the local level\textsuperscript{[113]}. In order to prevent excessive water accumulation in the GDL, a hydrophobic coating, usually polytetrafluoroethylene (PTFE), is applied. The portion of the GDL filled with water is determined by the lowest resistance pathways in terms of capillary pressure, which are tortuous and sometimes dead-ended, resulting in a non-optimal relationship between the water and gas transport characteristics (Figure 1). In a recent study of our group, we have shown that even though a high PTFE loading results in lower water content, the impact of this water is much higher than for materials with a moderate
PTFE loading and higher water accumulation\cite{54}. This emphasized the fact that not only the amount of water in the porous structure is important, but that its distribution is crucial and has to be controlled. The fundamental interest of GDLs with patterned wettability was highlighted by Utaka et al. using a stacked arrangement of alternating hydrophobic and hydrophilic gas diffusion layers and measuring the oxygen diffusivity through this arrangement\cite{68}. The impact of water saturation on diffusivity was shown to be clearly lower for this hybrid arrangement compared to experiments made with either purely hydrophobic or purely hydrophilic layers.

While the benefit of GDLs with defined water removal pathways is clearly established, none of the previous studies found in the literature proposed a method to produce such materials in a way compatible with mass production. In the broad sense, previous approaches can be categorized into three groups: first, the “perforation approach” was initially published by Gerteisen et al. and continued by other groups\cite{64,65,114}. This method consists of locally increasing the pore size within the GDL by either laser or mechanical perforation, which resulted in reduced mass transport losses when cylindrical holes were introduced into the GDL underneath the flow channels. A major drawback of this approach is the very limited design flexibility, in particular the impossibility of generating patterns for the improvement of in-plane transport properties. Second, the approach of “local coating” is based on the application of a hydrophobic coating to defined regions, leaving the remaining (carbon fibers) uncoated. Although this method was shown to be successful on small samples in terms of oxygen diffusivity improvement, it appears to have a rather limited scale-up potential\cite{69,115}. Third, the “surface and physical interaction” approach has only been reported in patented literature and is based on plasma induced surface modification of the GDL using patterns and deposition of solid hydrophilic particles (metal oxides)\cite{72}. Surface modifications in the range of 1 \( \mu \)m can preferentially relocate the water on the surface but the bulk properties remain unmodified\cite{21}. Deposition of solid oxide nanoparticles into the inner porosity appears difficult to implement and the lack of covalent bond chemistry may affect the durability.

We propose a material design consisting of defined patterned hydrophobic regions providing a dry, non-mass transport limited pathway (decreased tortuosity) for reactant gases to reach the catalyst layer. Intermittent hydrophilic regions of the proposed material provide a separate pathway for product water to leave the cell (Figure 3.1). A minimum feature size of 100 \( \mu \)m seems to be the reasonable target since for most carbon fiber papers this dimension corresponds to the size of 2-3 pores.
Figure 3.1 - Illustration of the relation between the pathways for liquid water (blue) and for reactant gases (green) in porous materials. Left: in standard hydrophobic materials. Right: in the new proposed material.

Here, we report a new fabrication method (Figure 3.2) based on radiation grafting for preparing novel GDL materials with patterned wettability properties. First, commercial GDLs are coated with a hydrophobic fluoropolymer. Then, they are locally exposed to an electron beam (using masks for pattern creation) in order to create radicals in the polymeric coating. Finally, they are immersed into solutions of hydrophilic monomers and graft co-polymerization occurs only in the regions previously exposed to the electron beam. One of the main advantages of the method lies in the realistic scale-up possibilities. Furthermore, modifications throughout the bulk of the GDL and tunable wettability offer significant advantages compared to previous approaches.[73]

Fluorinated ethylene propylene (FEP) was chosen as hydrophobizing agent. Contrary to the commonly used PTFE, FEP offers higher resistance to radiation[78] as well as stronger hydrophobicity and better reaction kinetics towards graft co-polymerization. We used N-vinylformamide (NVF) as a hydrophilic monomer leading to the graft-copolymer system FEP-g-NVF. Kinetic studies performed on flat FEP foils (25 µm) allowed finding synthetic conditions to lower the contact angle (CA) to values of 20±3° from initially 105±3°. Additionally, experiments were carried out with FEP foils in order to validate the pattern sizes and their spatial resolution. A high accuracy of pattern reproduction on the modified substrate was obtained (Appendix A, Figure 3.6).

II. Illustrations of the pore “detail” to show the modification occurring on the coating of the carbon fibers.

III. Illustration of the reaction “detail”.

Figure 3.2 - I. Synthesis method for the porous material with patterned wettability. (a): base porous material (hydrophobized). (b): irradiation using a mask. (c): locally irradiated base material. (d): imbibition with grafting solution. (e): resulting material with patterned wettability. II. Illustrations of the pore “detail” to show the modification occurring on the coating of the carbon fibers. III. Illustration of the reaction “detail”.

These conditions were then applied to the grafting reaction of NVF into the porous medium.

A GDL modified using the procedure described above is shown in Figure 3.3.a, after imbibing the material with water. The hydrophilic slits are clearly visible as water tends to accumulate in these regions. Elemental mapping with energy dispersive x-ray (EDX) spectroscopy was performed from the top (Figure 3.3.b) and bottom surfaces of the modified GDL. In spite of the irregular nature of the intensity signal due to the material roughness, it was found that the modified area (visualized by the presence of chlorine after forming the quaternary ammonium salt, see experimental section) is a sharp band on both surfaces (Figure 3.3.c), confirming that the electrons effectively activate the material throughout its thickness, and that their scattering does not result in an important loss of resolution.
As of now, EDX has been employed to indicate the presence of chemical modifications leading to hydrophilic regions; however the penetration depth of the technique is limited to several micrometers (on top and bottom surfaces). Similarly, optical visualization confirmed the preferential location of water on the surface of the material, but did not give information about the distribution in the inner pores of the material. For that reason, a setup was designed in order to precisely control the capillary pressure while measuring the local saturation of the porous material. Broadly speaking, water is pushed against the GDL and the response in terms of water redistribution is quantified using neutron radiography. This technique represents one of the most complete ex-situ characterization methods available because it contains information about the inner properties (pore size distribution and internal wettability)\[34\].

In the absence of capillary pressure (Figure 3.4.a, 0 mbar radiograph) no liquid water is present in the porous medium, except in the region adjacent to the injection channel. At 10 mbar (Figure 3.4.b) the hydrophilic lines appear partially filled. Larger pores in the low contact angle region are preferentially filled at lower pressures. At slightly increased
pressure, 20 mbar (Figure 3.4.c), the lines seem totally filled with saturation values of around 80% in the hydrophilic region and 20% in the hydrophobic domain. Lateral spreading is detected at 40 mbar (Figure 3.4.d), reaching saturation of around 100%, while the line broadens to around 400 µm width. Complete saturation of the material and therefore loss of structuring happens at around 50 mbar (Figure 3.4.e). The observed behavior already suggests a potential improved water removal within an operating fuel cell: liquid water will flow through the predefined hydrophilic regions towards the flow channels (and subsequently leave the cell) when low capillary pressures form, leaving dry hydrophobic regions for high gas diffusivity. This experiment, performed with water injection from a single channel in the middle of the GDL, is well representative of the in-plane transport necessary for the removal of water from under the ribs of an operating fuel cell.

![Capillary pressure experiment of a modified GDL](image)

Figure 3.4 - Capillary pressure experiment of a modified GDL (Toray 30%FEP 500-930 µm with NVF) measured with neutron radiography. The radiographs on top show water locations within the GDL with increasing capillary pressure: (a) 0 mbar, (b) 10 mbar, (c) 20 mbar, (d) 40 mbar and (e) 50 mbar. The graph below shows the quantified water thickness and saturation in a selected region for the different capillary pressures applied.

In order to investigate the performance achieved during operation using the modified materials, in-situ testing was carried out. The fuel cell setup used permits the simultaneous operation of 6 cells. The same gas mixtures including water vapor are fed
to all anodes and to all cathodes, but the gas flow is regulated individually for each cell using mass flow controllers placed downstream. Thanks to these features, materials comparison (cathodic GDLs) can be done in a highly reliable way. Polarization curves of three different materials are shown in Figure 3.5. As can be seen, in-house coated and commercially available PTFE treated GDLs exhibited quite similar performance. This was done in order to validate our coating procedure and to provide a baseline with a commercial product. The slightly improved performance obtained when comparing FEP and PTFE coated GDLs can be explained with: first, the increased hydrophobicity of the FEP coated GDL due to the intrinsically larger hydrophobicity of FEP ($\text{CA}_{\text{FEP}}=104\pm1^\circ$, while $\text{CA}_{\text{PTFE}}=99\pm1^\circ$) and higher coating load which leads to larger fraction of covered carbon fibers; and second, the differences in the coating procedure which imply different coating distribution throughout the thickness of the GDL. Interestingly, a substantial performance increase was observed for the GDLs with patterned wettability. Samples with 500 $\mu$m wide hydrophilic lines and 950 $\mu$m separation were used, with the direction of the hydrophilic lines perpendicular to that of the flow channels. A clear improvement in the region of the curve limited by mass transport (at current densities, $i > 0.6 \text{ A cm}^{-2}$) was observed for the modified samples. This result highlights the potential of the new proposed material to significantly improve the performance and reduce the flooding without the addition of a microporous layer (MPL).

Figure 3.5 - Polarization curves at 50°C, 100/30%RH anode/cathode of the following three materials: Toray TPG-H-060T commercial (Toray commercial) -1 cell-, Toray TPG-H-060 coated in-house with 30%wt. FEP (Toray 30% FEP) -2 cells- and Toray TPG-H-060 coated in-house with 30%wt. FEP and pattern-grafted (500 $\mu$m hydrophilic slits with 950 $\mu$m separation) with NVF (Toray 30% FEP –patterned-) –3 cells-. 
In summary, we presented here a novel method for producing GDLs with patterned wettability that improve fuel cell performance. Synthetic details were reported together with ex-situ chemical characterization technique (EDX) and capillary pressure studies combined with neutron radiography. The synthetic process confers the material with a tunable gradient of hydrophilic and hydrophobic properties depending on the polymer chemistry used (monomer and synthetic conditions). Additionally, full design flexibility is permitted while the modification takes place throughout the bulk (or any pre-selected depth by adjusting the electron energy) of the porous structure without affecting the mechanical properties of the material. One of the main advantages of this approach is that it could be realistically scaled up into a roll-to-roll production process.[116]

Porous structures such as GDLs, microporous layers (MPLs) and catalyst layers are of high relevance to the fuel cell community and can benefit from the presented approach. Beside of fuel cell application, other fields such as microfluidics, ink jet printing and water-oil separation face similar problems and could benefit from the presented technology in the future.[117-120]

### 3.2 Experimental Section

#### 3.2.1 Coating procedure

Commercially available carbon fiber papers (Toray TGP-H-060, 190 μm thickness) were coated with FEP. A dispersion of FEP (FEPD121 DuPont 55% solids) was diluted (1 part per 5 parts of water) and samples were slowly dipped into the coating solution for 60 seconds. Afterwards, they were placed horizontally on a needle-point holder to avoid gravitational effects and wicking coming from interfaces.[59]. Holders were placed in a vacuum oven and kept at room temperature for 60 min, afterwards the temperature was increased to 100°C and maintained for 60 min. This first thermal process allows for evaporation of water and traces of other solvents present. The heater was then switched off to allow for gentle cooling down of the sample. Samples were taken out and placed in a muffle oven at atmospheric pressure and two new temperature ramps were set: the first up to 260°C allows for evaporation of the surfactant (50 min ramp, 10 min plateau) and the second one up to 280°C allows for sintering of the polymer (20 min ramp, 20 min plateau). Coating loads of around 30% by weight were obtained and this process was proved to provide a homogenous distribution of the coating throughout the bulk of the GDL (Appendix A, Figure 3.7).
3.2.2 Irradiation

Low-energy electron beam treatment was carried out in an EBLab 200 sealed laboratory emitter system from Comet AG (Flamatt, Switzerland). Samples were subjected to a dose of 50 kGy under nitrogen (<200 ppm oxygen), employing an acceleration voltage of 200 kV at a conveyor speed of 12 m/min and an air gap of 10 mm.

For the patterned materials, 2 mm thick stainless steel masks were prepared with water jet (Waterjet AG, Aarwangen) with a pattern of 500 μm spaced 950 μm. The thinner lines were machined into 0.5 mm thick stainless steel sheets using a combination of laser and water jet (Synova, Lausanne) with a pattern of 100 μm spaced 500 μm. After electron beam treatment, samples were rapidly stored at -80°C to minimize radical recombination prior to grafting.

3.2.3 Grafting reaction

N-vinylformamide (NVF) was used as grafting monomer. Pure monomer (Sigma Aldrich 98%) was used as received. Cylindrical glass reactors (60 mL) were used at atmospheric pressure. The reactor chamber was deoxygenated by flushing with nitrogen (8 mL/min) for 60 min. Afterwards, reactors were placed into a water bath at 70°C to start the radical polymerization. The materials were then rinsed under vacuum by flowing 300 mL of ethanol, isopropanol and water in three consecutive cycles.

Hydrolysis and ion exchange with Cl⁻: This step is not part of the normal synthesis and was applied, for visualization purposes, only to the samples measured by energy dispersive X-ray. Samples were placed in a solution of 2M NaOH at 70°C during 5 hours for the hydrolysis of NVF to N-vinylamine (NVA). Afterwards, samples were placed in a solution of 0.1M HCl at room temperature overnight for forming the ammonium salt.

3.2.4 Microscopy

The scanning electron micrographs were recorded using a FE-SEM Ultra 55 (Carl Zeiss, Oberkochen, Germany). Energy dispersive X-ray analysis was performed using a compatible accessory (EDAX TSL, AMETEK). The elemental mappings presented here were taken with an acceleration voltage of 10 keV, an aperture of 60 μm and a gun-to-sample distance of 8 mm.
3.2.5 **Capillary pressure experiment**

The cell design is the same as the ones used for the in-situ characterization, except that only one central channel is used for water injection (1 mm width). The modified GDL was located with the hydrophilic lines perpendicular to the channel. A porous hydrophobic membrane (HVHP04700, Durapore) of 125 μm thickness was used as a separator. This allows having the gas equilibrated at atmospheric pressure; meanwhile it is impermeable for liquid water. Water pressure was controlled by regulating the height of a 30 L water vessel with a precision motor. A time of 10 minutes for each pressure point was allowed for equilibration. Neutron radiographs in through-plane configuration were taken during the complete duration of the imbition. Experiments were carried out at 25°C.

3.2.6 **Neutron imaging**

Images were recorded at the ICON beamline of the SINQ spallation source at the Paul Scherrer Institute\[98\]. Measurements were performed with a 20 μm Gd2O2S scintillator. The pixel pitch was 13.5 μm and the effective resolution (10% amplitude of the modulation transfer function), taking into account the blurring induced by the beam divergence combined to the sample-detector distance of 30 mm, was 9.1 line pairs per mm corresponding to a spatial resolution of 55 μm. A CCD camera (Andor DV436, 2048x2048 pixels) was used, with an exposure time of 30 s and a readout time of 8 s. All radiograms underwent noise filtering (3x3 median filter), correction of the beam and detector inhomogeneities, correction of the background contributions (detector background, neutrons scattered by the setup) and correction of beam intensity fluctuations\[121\]. According to the Lambert-Beer law, the water thickness can be calculated using a known attenuation coefficient of 4.5 cm\(^{-1}\) for the setup used. More details about the image processing can be found in the reference\[103\].

3.2.7 **In-situ testing**

The multicell setup described elsewhere\[15\] was used. Cells were machine into aluminum and nickel-gold coated. Flow fields have 5 parallel channels (0.55 mm depth and 1 mm width). The temperature was set to 50°C and the relative humidity (RH) of anode and cathode were set to 100% and 30% respectively. Fixed gas flow rates of 0.4 NL·min\(^{-1}\) and 1.0 NL·min\(^{-1}\) were used for the anode and cathode, respectively, translating to very high stoichiometries (> 60 at a current density of 1 A·cm\(^{-2}\)) corresponding to the “differential cell” concept\[54\]. The cells were operated with increasing current densities. The hold time for each data point was fixed to 15 minutes.
A catalyst coated membrane (CCM) (Primera 5710, W.L. Gore & Associates, Inc., USA) was used with Pt-loadings of 0.1 mgPt·cm⁻² and 0.4 mgPt·cm⁻² on anode and cathode, respectively. Three cells were built with Toray 30%FEP pattern-grafted (cathode) and Toray 30% plain (anode); two cells contained Toray 30% plain (cathode) and Toray 30% plain (anode); and one cell contained Toray TPG-H-060T commercial (anode and cathode). The GDL compression rate was set to 20%. The Toray 30% FEP plain and Toray 30% FEP grafted are both obtained from the same batch of in-house coated materials.
3.3 Appendix A – Supplementary Information

3.3.1 Comments on resolution achievements

As described in the main document, patterned steel masks were used to selectively stop the electrons and to define activated stripes. The electrically conductive carbon fibers composing the GDL are expected to cause scattering (as sketched in Figure 3.6). Consequently, an acceptable resolution needs to be verified. For this purpose, we built two setups that allow comparing the resolution of the activation when a GDL is present (Figure 3.6). The difference between both configurations shows the diffractive effect of GDL. The results prove that there is not significant “resolution loss” effects (at energies of 1.5 MeV).

![Figure 3.6 - Top: illustration of the setup used in the resolution experiment (combination of mask-FEP film to study the activation when no GDL is present-left- and combination of mask-GDL-FEP film to study the activation behind the GDL-right). Bottom: Results of the resolution check-out.](image)

3.3.2 Comments on coating distribution throughout the GDL

One of the main advantages of the presented approach is that a modification through the plane can be produced, helping this to channel the water from catalyst layer to flow fields. However, in order to achieve that, the polymeric coating needs to be accordingly distributed throughout the bulk of the material (covering the whole thickness).
Some studies found in literature pointed at this issue and evidenced the effect of drying time and application of vacuum in the coating distribution\cite{58, 59}. With the thermal process used (described in the Experimental Section) we achieved an homogenous distribution of the coating as characterized by EDX of the fluorine signal on a cross section (Figure 3.7), when using vacuum and atmospheric pressure in the initial drying step. The benefit of using vacuum is not striking in Figure 3.7. A good distribution can be obtained by tuning drying temperature and time, but this is not the scope of our work, as coating procedures are already part of the “mainstream” GDL production.

*Figure 3.7* - Toray TPG-H-060 with 30%FEP with two different coating processes: applying vacuum in the first drying step (left) and drying at atmospheric pressure (right). Fluorine elemental mapping (EDX) is shown in the top row and secondary electron micrograph in the bottom row.
Chapter 4. Tuning the wettability – from flat to porous systems

In this chapter a thorough systematic study is presented on synthesis and characterization of hydrophilic surfaces which have been prepared using the radiation grafting method. We start by performing radical polymerization on flat substrates (model system) to find successful experimental conditions to prepare hydrophilic surfaces after short reaction times. Two co-polymer systems are evaluated: N-vinylformamide and acrylic acid.

In the first part, grafting and characterization of wettability and chemical composition is performed on flat films. Later, a similar procedure is applied to porous GDLs and the apparent wettability is correlated with the estimated intrinsic wettability. In the last part, a preliminary study on thermal stability is presented. In the present chapter, materials are homogenously modified (i.e. without patterns).

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4.1 Abstract

A novel type of fuel cell gas diffusion layer with patterned wettability is herein reported. The production of hydrophilic patterns by radiation grafting depends on two main steps: electron beam activation and polymerization reaction. In this first part of the series, we are giving extensive details about the synthetic routes for modifying porous media’s wettability. Two monomers (acrylic acid and N-vinylformamide) were used for the hydrophilization of the fluoropolymer and a parametric study was performed. Finally, a preliminary thermal degradation study was carried out.

We found conditions to produce hydrophilic gas diffusion layers with short reaction times (about 10 minutes) and proved that the synthetic method is suitable for creating local modifications. For hydrophilic surfaces, the coating load significantly impacts wetting dynamics.

4.2 Introduction

At the end of 2014, automotive polymer electrolyte fuel cells (PEFCs) began to be commercialized[122, 123]. The fuel cell industry grew from $1.3 billion to $2.2 billion in one year’s time (from 2013 to 2014)[124]. Due to the absence of pollutant emissions and their high efficiency, fuel cells represent a very promising power source for portable and mobile applications. However, cost reduction and improvement of long term stability remain as bottlenecks. The US Department of Energy (DOE) estimated a current system cost at large production volumes of 53 $/kW, the target being 40 $/kW for 2020 and the ultimate target 30 $/kW[10]. Besides the obvious route of reducing the material costs (e.g. amount of precious metal catalyst)[125], the increase of power density would also result in a cost reduction for a system of a specified total power.

The water management within PEFCs is rather complex. While some water is needed in order to provide proton conductivity to the polymeric membrane and ionomer in the catalyst layer, excessive water accumulation in the diffusion layers (DLs) limits the gas transport to the catalyst layers (CL), resulting in mass transport losses limiting the power density. At the cathode side, liquid water is transported by capillary forces from the CL through the gas diffusion layer (GDL) towards the flow field channels in order to be removed from the cell. The combination of pores providing the lowest capillary pressure (larger pores and more hydrophilic ones) define the pathways for water flux inside GDLs[28, 11]. Consequently, the microstructure and local surface energy of the GDL directly impact the gas-liquid transport characteristics.
Commerci ckally available GDLs are highly porous carbon fiber paper or cloth materials. The pristine arrangement of fibers is typically coated with a hydrophobic polymer to increase its water repellency and reduce flooding. Polytetrafluoroethylene (PTFE) is the most commonly used polymer, followed by fluorinated ethylene propylene (FEP) \[80\]. The effect of the addition of such coating has been extensively studied and optimal coating loads have been found for different GDLs\[53, 54, 126\]. The application of hydrophobic coatings on GDLs is usually done by “dip coating” techniques, which include the immersion of carbon substrates in water-based dispersions of fluoropolymer particles followed by a thermal treatment to evaporate the solvents and sinter the polymer. The impact of the thermal treatment onto the final coating distribution and its influence on permeability and performance has also been studied \[56-60\]. Additionally, it is known that agglomerates of the coating material appear in different locations (such as carbon fiber intersections) and a notable fraction of carbon surfaces remain uncoated. To tackle this issue, novel coating techniques targeting the application of a homogeneous “monolayer” with hydrophobic character were reported. Thomas et al. published a method to produce superhydrophobic GDLs by electrochemical reduction of diazonium salts in liquid phase\[61\]. They demonstrated the presence of homogeneously distributed and covalently bound hydrophobic compounds on the GDL surface. Van Nguyen et al. reported a method to provide a more uniform and durable coating by direct fluorination\[62, 63\]. In this approach, fluorine gas reacts with the carbon to create a wet-proof surface. These two novel approaches do not significantly affect the morphology of the porous media (by, for example, reducing the average pore diameter) and have shown improved operando performance. However, none of these techniques provides optimally localized routes for liquid water transport. The water transport is thus defined by the lowest capillary pressure pathways, which are often tortuous. The oxygen in the air diffuses in opposite direction, and is therefore forced to travel longer distances. These two contradictory requirements provide suboptimal liquid-gas transfer characteristics within the cell using state-of-the-art GDLs.

A possibility to engineer the water transport within the GDL is based on artificially creating pathways for water removal, leaving the remaining regions free of water for improved gas diffusion. Several approaches going in this direction have been reported in the literature. Some groups reported performance improvements when perforating the GDL (by laser or mechanically) under the channel area\[64, 65, 127\]. Even if a lower mass transfer resistance was measured under certain conditions, this approach suffers from design limitations, such as the impossibility of creating elongated pathways due to the impact on the mechanical integrity of the GDL. Koresawa et al. presented a method to locally apply a hydrophobic coating, leaving the remaining regions uncoated \[69, 118\].
Tuning the wettability – from flat to porous systems

While increased oxygen diffusivities were obtained at different saturation levels, the production of such a material appears difficult. Protected technologies include the use of plasma sources to produce oxide groups near the external surfaces of the GDL [71]. By doing so, the GDL surface becomes hydrophilic but the inner surfaces remain untreated. Recently, a technique was patented in which hydrophilic oxide metal particles are added in localized regions [72]. Even if these approaches have the potential to create hydrophilic pathways, some concerns regarding their durability and, more important, the realistic scale-up possibilities still remain.

Recently, we have developed a method to produce GDLs with patterned wettability by means of the radiation grafting method [73]. Radiation grafting is a promising method for modification of polymers [128, 129]. One prominent application has been the grafting of fluoropolymer films to produce proton conducting membranes for fuel cells [22]. Generally speaking, a low-cost structural polymer is modified by addition of a second polymer constituent which contributes a specific functional property.

The application of the radiation grafting method for GDLs is based on locally modifying the polymer coating in order to make it hydrophilic (therefore lowering the contact angle). Its main steps are: first, coating the material following the classical dip-coating procedure with FEP (due to its superior radiation resistance, faster kinetics and higher hydrophobicity compared to PTFE); second, exposing the material to an electron beam using masks to selectively block the radiation; third, exposing the irradiated material to a hydrophilic monomer solution to initiate the grafting polymerization in the activated regions [74]. Consequently, the final material has a clearly defined hydrophilic pattern, while the rest remains hydrophobic (original FEP coating).

Recently, we have demonstrated the successful synthesis of these materials to yield water-filled patterns at low capillary pressures (around 10 mbar), meanwhile the hydrophobic regions remain free of water up to significantly higher pressures (around 40 mbar). Furthermore, improved fuel cell performance was obtained when comparing modified with baseline materials, especially at high current densities, where mass transport limitations become dominant [29].

Here, we present a comprehensive study on the synthesis and characterization of GDLs with patterned wettability. In the first part of a series of three publications, we focus on the elaboration of synthetic conditions to control the final wettability of the material. To do so, we first identify suitable treatment conditions using flat FEP films (Figure 4.1) to later adopt the synthetic route for GDLs. The treated materials are then characterized in terms of their chemical features and their wettability and closes with a preliminary thermal degradation study. In order to synthesize samples for extensive characterization,
plain areas samples are used, whereas the subsequent papers will focus exclusively on materials with patterned wettability. We will complement this work with a second part showing the impact of material characteristics (substrate, amount of coating, grafting chemistry, pattern design) on the water distribution as a function of capillary pressure, while the third part of the series will focus on the in situ testing of the synthesized materials.

4.3 Experimental

4.3.1 Methodology

One of the important advantages of the synthetic method is the potential of tuning the final wettability. By varying the synthetic conditions (type of monomer, concentration, reaction time or temperature) radiation grafting offers the possibility to obtain the desired properties, i.e. a hydrophilic surface, without sacrificing its mechanical integrity. Unfortunately, the rough nature of the GDL surface and its heterogeneity result in a complex relation between the observable external contact angle and the intrinsic contact angle. This will be addressed in detail in the “Results & Discussion” section.
The contact angle being a surface property of a material, the modifications of this parameter by radiation grafting reported in the literature use radiation sources activating the surface only (e.g. plasma or UV). However, using these techniques on porous GDLs would probably lead to notable shadow effects since only external surfaces would be activated, leaving the inner porosity unaffected. For that reason, penetrating radiation, such as MEV electrons, is chosen. The activation using electron radiation produces radicals throughout the complete material thickness. The grafting polymerization initially starts on the external surfaces of the activated polymer, diffusing then into the bulk to copolymerize with polymer chains in the bulk of the material. Nevertheless, our target is to graft only on the polymer surfaces[74], as it is known that bulk grafting processes lead to brittle materials[130]. Consequently, these two contradictory requirements (using a bulk activation radiation but graft only on the surface) need to be fulfilled by adjusting the synthetic conditions.

For acrylic acid grafted on FEP, this diffusion process has been well studied. Hegazy et al. reported the grafting kinetics at different dose rates and acrylic acid concentrations in water[131]. In a subsequent publication from the same researchers, X-ray micrographs showed the grafting penetration in the FEP film[130]. Some of the relevant findings were: (a) the lower the dose rate, the deeper the grafting proceeds. Therefore, at high dose rate graft polymerization dominates over monomer diffusion into the bulk, leading to more pronounced surface grafting. (b) The crystallinity of the polymer increases upon irradiation. (c) At lower monomer concentrations the grafting proceeds more deeply into the base polymer and yields a homogeneous distribution. We selected a relatively high dose in order to minimize the penetration of grafting, yet sufficiently low to avoid dramatic deterioration of mechanical properties[78].

In order to simplify the analysis of wettability and synthetic conditions for grafting, we decided to initially use FEP polymer films as a model system (Figure 4.1). Since the hydrophilization treatment of our method is based on only coating modifications, it can be assumed that carbon fibers remain unaltered. Attending purely to wettability changes, it is more convenient to use flat surfaces where Young’s relation applies and comparisons are straightforward since roughness effects are absent[29].

The following co-polymer systems were systematically studied: acrylic acid (AA) grafted onto FEP (FEP-g-pAA) and N-vinylformamide (NVF) grafted onto FEP (FEP-g-pNVF). The corresponding reaction schemes are shown in Figure 4.2. While AA is a well-known low-cost compound, NVF offers the possibility to extremely decrease the contact angle and produce a “fully-wetting” surface[132]. A parametric study including the effect of monomer concentration and reaction time was performed for both
systems. The modified polymeric films were characterized in terms of the mass increase (gravimetric degree of grafting), infrared spectroscopy and the surface wettability.

Figure 4.2 - Reaction schemes showing the two chemistries reported in this paper.

After successfully investigating synthetic conditions for lowering the contact angle, the reactions were carried out in porous media (Figure 4.1). The porous nature of the GDL and its hydrophobicity bring an additional requirement: the grafting solution must wet the inner pores, while simultaneously preventing air from being trapped inside. Different approaches were investigated, such as the use of solvents with a low surface
tension, the addition of surfactants in the grafting solution, or the introduction of the grafting solution under vacuum. We chose the last of the three approaches for most of the laboratory experiments with the AA grafting solution. The NVF grafting solution was found to readily wet the GDL, so no particular application strategy was necessary. In order to quantify the grafting reaction yield, energy dispersive X-ray analysis (EDX) and X-ray photoelectron spectroscopy (XPS) measurements allowed for the identification of the grafted compounds on the polymeric coating on the GDLs and to quantify the grafting kinetics.

Additionally, the final wettability of the modified GDL was investigated. For the sake of experimental simplicity, external contact angles on GDL surfaces were measured. The effect of reaction time on GDL wettability was investigated at a fixed coating load. Furthermore, the effect of the coating load at fixed reaction conditions was also studied.

Finally, we performed preliminary experiments to evaluate the thermal durability of the modified materials. State-of-the-art diffusion media for PEFCs are generally composed of a stack of a GDL with a microporous layer (MPL). The application of a MPL on the modified GDL would, in the worst case scenario, expose the material to an elevated temperature atmosphere, such as the polymer sintering temperature (270°C for FEP)\textsuperscript{[50]}. While several studies reported in the literature addressed GDL focused on mechanical degradation\textsuperscript{[133, 134]} and few studies on chemical degradation\textsuperscript{[135-137]}, no study has focused on thermal degradation. In standard materials composed of carbon fibers and the polymer coating the consequences are less critical at the given temperature range (slightly above the glass transition point). Partial melting of the polymer and soft oxidation of carbon fibers is to be expected. However, the changes induced by thermal stress on the grafted compounds can become very relevant. Therefore we perform this preliminary study of thermal stability in which special attention is taken to the influence on wettability.

Since the GDL entails additional complications to the understanding of degradation suffered by the different components (carbon fibers, binder and coating/grafted coating), we studied the effects of thermally degrading the model system (modified FEP films) at two different temperatures (100°C and 270°C). The first represents a realistic fuel cell operating temperature, while the second is the melting temperature of FEP. Thermogravimetric measurements shed light on the major degradation intervals, while a combination of infrared spectrometry with wettability measurements helped in understanding the degradation mechanism and its final effect on surface hydrophobicity.
4.3.2 Polymer FEP films

Fluorinated ethylene propylene (FEP) films were purchased from DuPontTM (Teflon® FEP Fluoroplastic Film Gauge 100). They have a thickness of 25 µm and an approximate area factor of 18 m²·g⁻¹. The films were cut to the desired sizes and cleaned with ethanol. Afterwards, they were dried under vacuum and stored in sealed bags prior to irradiation.

4.3.3 Gas Diffusion Layers

For all experiments reported here Toray paper (TGP-H-060) was used as a base material. It has a thickness of 190 µm, a bulk density of 0.44 g·cm⁻³ and a porosity of approximately 78%[138]. The material was then coated with FEP using the “dipping” method followed by a thermal treatment. The details of the coating application are described in an earlier publication[74]. For the work presented here, coating loads of 5%, 15%, 30%, 50% and 70% (relative to the carbon weight) were used.

4.3.4 Electron beam activation

A linear accelerator was used at LEONI Studer (Däniken, Switzerland) with a variable accelerator voltage of 1.05-2.35 MeV, a beam current in the range of 0 to 35 mA and a scan width of 1220 mm. Materials were mounted on metallic trays that were conveyed into the irradiation chamber. Conveyor speed [m/min] and beam current [mA] were adjusted accordingly to control the dose, which is the mean energy absorbed by matter per unit mass. Paper cardboard of 4 mm thickness was placed between the metallic tray and samples to reduce the backscattering. Energy of 2.1 MeV and a dose of 50 kGy were used in every case herein reported.

4.3.5 Reactants

Acrylic acid (Sigma Aldrich 99% containing 180-200 ppm MEHQ as inhibitor) was used as received. The monomer was diluted in water down to the desired concentration. When specifically stated, mixtures of acrylic acid (AA) with hexane were also used.

N-vinylformamide (Sigma Aldrich 98% containing 22-55 ppm 4-hydroxy-TEMPO as stabilizer) was used as received. The monomer was diluted in water down to the desired concentration or used pure.
4.3.6 Reaction of FEP films

FEP films were placed in cylindrical glass reactors (volume around 70 mL) together with the grafting solution at atmospheric pressure. To de-oxygenate the reaction medium, the grafting solution was purged with N\textsubscript{2} (flowrate of 8 NL\textcdot min\textsuperscript{-1}).

<table>
<thead>
<tr>
<th>Copolymer System</th>
<th>Monomer Conc. [%wt. in water]</th>
<th>Temperature [°C]</th>
<th>Time [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FEP-g-pAA</td>
<td>5, 15, 30</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>FEP-g-pAA</td>
<td>15</td>
<td>60</td>
<td>10, 30, 50, 70</td>
</tr>
<tr>
<td>FEP-g-pNVF</td>
<td>20, 40, 60, 80, 100</td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td>FEP-g-pNVF</td>
<td>80</td>
<td>70</td>
<td>10, 30, 50, 70</td>
</tr>
</tbody>
</table>

Table 4.1 summarizes the experimental conditions (monomer concentration, temperature and reaction time) used for the radical polymerization onto FEP films. After the reaction, samples were immersed in ethanol and isopropanol in two consecutive cycles overnight. Finally, they were dried under vacuum at 60°C before further treatment for characterization purposes.

4.3.7 Reaction in porous GDLs

A summary of the experimental conditions (chemistry used, coating load and reaction time) used for GDL grafting is shown in Table 4.2. GDLs were grafted using two different types of reactors. For carrying out the Toray FEP-g-pAA synthesis, a stainless steel reactor (50 mL volume) was used, allowing the introduction of the grafting solution under vacuum. Figure 4.3 shows a detailed diagram of the experimental setup for the AA grafting on GDLs. Initially N\textsubscript{2} was bubbled through the solution storage compartment for 60 minutes (3) as well as the reaction chamber (1) (lines a, b and c). Later, valve 7 was closed until a pressure of 50 mbar\textsubscript{abs} was attained in the reaction chamber and in lines a and c with the help of a vacuum pump. After closing valve 6 and slightly opening valve 7, a volume of 40 mL of monomer solution was sucked through line b into the reaction chamber (at a rate of about 20 mL\textcdot min\textsuperscript{-1}). Finally, valve 7 was closed to isolate the chamber. The reaction was initiated by placing the reactor in a temperature controlled bath at 60°C.
Table 4.2 - Summary of experimental conditions used in the grafting studies carried out on FEP coated GDLs.

<table>
<thead>
<tr>
<th>Copolymer system</th>
<th>Coating load [%wt. FEP]</th>
<th>Time [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toray %FEP-g-pAA</td>
<td>0, 5, 15, 30, 50, 70</td>
<td>60</td>
</tr>
<tr>
<td>Toray %FEP-g-pAA</td>
<td>30</td>
<td>0, 5, 15, 30, 45, 60, 120</td>
</tr>
<tr>
<td>Toray %FEP-g-pNVF</td>
<td>0, 5, 15, 30, 50, 70</td>
<td>60</td>
</tr>
<tr>
<td>Toray %FEP-g-pNVF</td>
<td>30</td>
<td>0, 5, 15, 30, 45, 60, 120</td>
</tr>
</tbody>
</table>

Figure 4.3 - Vacuum reactor setup used for the preparation of FEP-g-pAA in porous GDLs. The different elements are numbered as: (1) grafting reactor body; (2) GDL sample(s); (3) monomer solution vessel; (4) vacuum pump; (5) cold trap (condenser); (6) 3-way valve; (7) flow regulation valve.

4.3.8 Thermal degradation

The following samples were prepared in order to perform the thermal stability tests: an FEP film grafted with AA (15% wt. in H₂O) during 30 minutes; the very same after sodium exchange using NaOH 0.05M during 8 hours at room temperature; an FEP film grafted with NVF (80% wt. H₂O) during 30 minutes. The same FEP-g-pNVF was reacted with 2 M NaOH during 8 h at 80°C for the hydrolysis to the amine, FEP-g-pVAm. A piece of this new sample was then exposed to 0.025 M HCl during 8 h at room temperature for the formation of the quaternary ammonium salt, FEP-g-pVAmCl.

A punched-out piece of each sample was subjected to thermogravimetric analysis (TGA) for a first understanding of the thermal degradation profile. Further pieces of
each material were exposed to the following temperature programs: 2 hours at 100°C, 15 min at 270°C and 2 hours and 270°C. Afterwards, samples were cooled down and their water contact angles were measured.

### 4.3.9 Degree of grafting

The gravimetric degree of grafting (DG) was calculated for polymer films as the percentage of mass increase due to the grafting polymerization. The formula used was:

\[
DG(\%) = \frac{m_f - m_0}{m_0} \times 100
\]  

(4.1)

in which \(m_0\) is the initial mass of the dry polymer film (before activation and reaction) and \(m_f\) is the mass of the dry reacted polymer film (after cleaning). The gravimetric DG of the porous GDLs could not be measured since the mass increase due to grafting was below the detection limit of the balance.

### 4.3.10 Contact angle (CA) measurements

The measurements of the external contact angle on films were performed using an in-house built goniometer at atmospheric temperature. The droplet volume was 2 \(\mu\)L in every case. At least 5 droplets were measured per sample and the contact angle was obtained by averaging these measurements. The measurements on modified GDLs were also undertaken following the same procedure.

For the measurements of wetting dynamics, a commercial device (OCA 25 Dataphysics) was used, with a volume of 2 \(\mu\)L equipped with a CCD camera with 34.5 fps. At least 4 repetitions per sample were taken. The image processing was done with a commercial software (SCA 20, Dataphysics) using ellipsoidal fitting to extract the remaining volume at each frame. From that information, the absorbed volume can be easily extracted:

\[
V_{abs} = V_0 - V_{remaining}
\]  

(4.2)

Since the initial volumes, \(V_0\), for each repetition differ, the absorbed volume, \(V_{abs}\), was normalized to the initial volume for comparative purposes. The normalized absorbed volumes for each repetition were averaged at each time frame and its standard deviation and confidence interval (at a 99% confidence level) were calculated.

### 4.3.11 Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were recorded using a Vertex 70v FTIR spectrophotometer (Bruker). Spectra were acquired under vacuum at 4 cm\(^{-1}\) resolution between 400 and 4000 cm\(^{-1}\).
Attenuated total reflectance (ATR) spectra were measured using a horizontal ATR accessory with a ZnSe crystal at 45° angle of incidence. The OPUS software was used for the baseline subtraction.

Table 4.3 summarizes the peaks used for quantification in both modes (transmission and ATR). The transmission peaks were normalized to the C-F deformation absorption band integrated between 583-685 cm\(^{-1}\)[139], while the ATR bands were normalized to the C-F stretch integrated between 1170-1340 cm\(^{-1}\) as indicated in the table 4.3.

<table>
<thead>
<tr>
<th>System</th>
<th>Mode</th>
<th>Peak position [cm(^{-1})]</th>
<th>Characteristic vibration</th>
<th>Integration domain [cm(^{-1})]</th>
<th>Integral indicator</th>
</tr>
</thead>
<tbody>
<tr>
<td>FEP-g-pAA</td>
<td>Trans</td>
<td>2605 &amp; 3062</td>
<td>C-H(<em>\alpha) &amp; O-H(</em>\alpha)</td>
<td>2210-2850</td>
<td>I(_{\text{CH}2+\text{OH}2})</td>
</tr>
<tr>
<td></td>
<td>Trans</td>
<td>1457</td>
<td>C-H(_\delta)</td>
<td>1380-1490</td>
<td>I(_{\text{CH}6})</td>
</tr>
<tr>
<td></td>
<td>ATR</td>
<td>1720</td>
<td>C=O(_\alpha)</td>
<td>1600-1800</td>
<td>I(_{\text{CO}2})</td>
</tr>
<tr>
<td>FEP-g-pNVF</td>
<td>Trans</td>
<td>2920 &amp; 3274</td>
<td>C-H(<em>\alpha) &amp; N-H(</em>\alpha)</td>
<td>2655-3725</td>
<td>I(_{\text{CH}2+\text{NH}2})</td>
</tr>
<tr>
<td></td>
<td>Trans</td>
<td>1548</td>
<td>N-H(_\delta)</td>
<td>1460-1590</td>
<td>I(_{\text{NH}6})</td>
</tr>
<tr>
<td></td>
<td>ATR</td>
<td>1388</td>
<td>C-N(_\alpha)</td>
<td>1450-1750</td>
<td>I(_{\text{CN}2})</td>
</tr>
<tr>
<td>Both (normalization)</td>
<td>Trans</td>
<td>627 &amp; 636</td>
<td>C-F(_{\text{def}})</td>
<td>583-685</td>
<td>I(_{\text{CF}2}) [139]</td>
</tr>
<tr>
<td></td>
<td>ATR</td>
<td>1149 &amp; 1204</td>
<td>C-F(_\alpha)</td>
<td>1170-1340</td>
<td>I(_{\text{CF}2})</td>
</tr>
</tbody>
</table>

### 4.3.12 Energy-dispersive X-ray spectroscopy (EDX)

A scanning electron FE-SEM Ultra 55 microscope (Carl Zeiss, Oberkochen, Germany) was used. Energy dispersive X-ray analysis was performed using a compatible accessory (EDAX TSL, AMETEK). The elemental mappings presented here were taken with a voltage of 8 keV, aperture of 60 \(\mu\)m and a gun-to-sample distance of 9 mm. Two different spots (with an approximate area of 1 mm\(^2\)) were measured per sample and averaged.
4.3.13 X-ray photoelectron spectroscopy (XPS)

XPS measurements were carried out with a VG ESCALAB 220iXL spectrometer (Thermo Fisher Scientific) using monochromatic Al Kα x-ray radiation (1486.6 eV) with a beam size of \( \sim 500 \, \mu \text{m}^2 \) (power of 150 W). The spectrometer was calibrated using the Ag 3d_5/2 peak at the binding energy (BE) 368.3 eV. The pressure in the analysis chamber was about \( 2 \times 10^{-9} \, \text{mbar}_\text{abs} \). The spectra were recorded in constant analyzer energy mode at a pass energy of 30 eV. The binding energy calibration was done based on the C-C (GDL) peak at 284.5 eV.

4.3.14 Thermo-gravimetric analysis (TGA)

A Perkin Elmer TGA 4000 device was used with the following temperature program: the temperature was initially held at 50°C for 5 minutes, and then increased from 50°C to 800°C at a rate of 10°C·min\(^{-1}\). A continuous air flow of 20 mL·min\(^{-1}\) was applied.

4.4 Results and Discussion

4.4.1 Grafting on polymer films

As we require a surface modification induced by a bulk penetrating radiation, we first performed studies on polymer films to investigate to which extent this is possible. Additionally, we investigate synthetic conditions to produce hydrophilic surfaces at reaction times as low as possible while reducing the complexity of the analysis. Considering the FEP-g-pAA system, the degree of grafting increases fairly linearly with the monomer concentration (Figure 4.4.a), but the contact angle does not increase much for concentrations higher than 15%wt. It was also found that concentrations above this limit led to significant formation of homopolymer. Therefore a concentration of 15%wt. was used for the analysis of grafting kinetics. After reacting for 30 minutes, a degree of grafting of 120% was reached (Figure 4.4.b), resulting in a contact angle decreased to 55° (from an initial value of around 110°). A nearly linear increase of the degree of grafting as a function of the reaction time was observed for the first hour of reaction, after which it tends to stabilize around 200% (meaning a threefold increase in weight). The contact angle decreases slightly but after the minimal contact angle is already nearly reached at 30 minutes (Figure 4.4.c).
A different grafting behavior was observed for the FEP-g-pNVF. The monomer concentration at a fixed reaction time has a very large impact on the DG, with very little grafting at concentrations below 60%wt. and a sharp increase above this threshold (Figure 4.4.d). The minimum contact angle is reached for 80%wt. and any further increase of the concentration leads to a massive increase in the DG. Therefore, the monomer concentration of 80%wt. was chosen as a compromise between low contact angle and moderate degree of grafting and used for the subsequent analysis of grafting kinetics. In contrast to that of AA, the grafting of NVF (Figure 4.4.e) reaches a nearly stable value after less than 15 minutes (both in terms of degree of grafting and of contact angle), providing hydrophilic surfaces with CAs of around 20° (Figure 4.4.f). The grafting kinetics might even be faster, but the time necessary for the reactor to heat up does not allow measurements at shorter time scales. Infrared heating or the use of pre-heated grafting solutions would be expected to shift the degree of grafting to higher and the contact angle to lower values, especially at short times.
The lowest achievable contact angle was identified to be around 50° for FEP-g-pAA and 20° for FEP-g-pNVF, respectively (Figure 4.4). Hydrolyzing the FEP-g-pNVF to produce FEP-g-pVAm did not significantly lower the contact angle, which justifies our decision to work with the formamide form. These results are in good agreement with previous reports about grafting the same monomers onto ETFE films using plasma [33].

The differences observed suggest that the FEP-g-pAA system is strongly prone to bulk grafting – as shown by the strong increase of the degree of grafting – and the FEP-g-pNVF system rather exhibits surface grafting. To confirm this, the modified films were investigated by FTIR in two different configurations: in transmission mode, which is sensitive to the entire thickness of the material, and in ATR mode, which is only sensitive to a few micrometers below the surface.

![Figure 4.5 - ATR-FTIR spectra. a: comparison of pristine FEP, FEP-g-pAA, and FEP-g-pAA-Na⁺; b: comparison of pristine FEP, FEP-g-pNVF, and FEP-g-pVAm; c: detailed comparison of FEP-g-pAA and FEP-g-pAA-Na⁺; d: detailed comparison of FEP-g-pNVF and FEP-g-pVAm.](image)
Figure 4.5 contains FTIR-ATR spectra proving the presence of the desired chemical groups. For FEP-g-pAA (Figure 4.5.a and 4.5.c), there is an important carbonyl stretch peak (C=O) appearing at 1720 cm$^{-1}$. There are also two broad absorption bands at 2605 and 3062 cm$^{-1}$, characteristic of C-H and O-H stretch vibrations, respectively. The sodium polyacrylate salt (FEP-g-pAA-Na$^+$) is clearly distinguishable because of its two absorption bands at 1426 and 1584 cm$^{-1}$ that are shifted to lower wavenumbers compared to the corresponding bands in FEP-g-pAA.

FEP-g-pNVF (Figure 4.5.b and 4.5.d) is characterized by a C=O stretch peak at 1683 cm$^{-1}$ (amide I). N-H (amide II) in-plane bending and C-N stretch peaks occur at 1548 and 1388 cm$^{-1}$. Additionally, a weak C-H bending band at 1442 cm$^{-1}$ and a broad N-H stretch band around 3274 cm$^{-1}$ are observed. In combination these peaks prove the presence of formamide groups in the polymer structure. FEP-g-pNVF hydrolysis yielding FEP-g-pVAm is strongly suggested by the disappearance of the C=O and N-H stretching bands that is accompanied by the appearance of an NH2 stretching band at 1572 cm$^{-1}$.

Having discussed the most notable molecular vibrations, we quantitatively compare the signals obtained for relevant peaks in transmission and ATR modes (Figure 4.6). In transmission mode, the normalization of the integrated peaks of representative chemical groups (C=O, O-H and C-H for FEP-g-pAA and N-H, C-H and C-N for the FEP-g-pNVF) showed interesting trends. The obtained ratios (cf. Experimental) are in very good agreement with the gravimetric degree of grafting characterization (Figure 4.4.b and 4.4.c). The grafting kinetics of FEP-g-pAA (using two indicators) showed a gradual increase of acrylate-related groups over reaction time; a plateau is reached after 70 min (Figure 4.6.a). The increase of formamide-related species (indicator of FEP-g-pNVF) reaches a plateau after 30 minutes (Figure 4.6.c).

The normalized integrated ATR peaks show trends that are different from those obtained in transmission mode. In the case of FEP-g-pAA, a maximum is reached after 50 minutes (Figure 4.6.b). For the FEP-g-pNVF, a plateau is reached already after 10 minutes of reaction (Figure 4.6.d). These trends are very similar to the variation of contact angle over reaction time for both systems (Figures 4.4.c and 4.4.f), which could be explained by the fact that the contact angles are influenced by the amount of chemical species on the external surfaces. The comparison of the results obtained via quantified infrared spectroscopy (using transmission and ATR modes) and gravimetric degree of grafting combined with contact angle measurements supports the theory that FEP-g-pAA grafting diffuses towards the bulk while FEP-g-pNVF grafts on the external surfaces.
4.4.2 Grafted GDLs: chemical characterization

Gravimetric quantification of the degree of grafting was not possible in the modified GDLs due to the insufficient change of weight. In order to have an indicator for the degree of grafting in GDLs, two different methods were employed: EDX and XPS. For the FEP-g-pAA system, the degree of grafting using EDX was measured as the ratio of the oxygen (O) and fluorine (F) signals, assuming that these elements are exclusively found in the grafted poly(acrylic acid) and in the base fluoropolymer, respectively. For FEP-g-pNVF, the same principle was used, but using nitrogen (N) as an element characteristic of the grafted compound.

The shapes of the kinetic curves are consistent with those obtained for polymer films. While the FEP-g-pAA (Figure 4.7.a) system shows a continuous increase of grafting
over time, the FEP-g-pNVF (Figure 4.7.b) system reaches a plateau after 15-30 minutes of reaction time.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4_7.png}
\caption{Grafting kinetics quantified with EDX. \textit{a}: Toray 30\%FEP-g-pAA; \textit{b}: Toray 30\%FEP-g-pNVF.}
\end{figure}

While the EDX analysis is limited to the identification of different elements, XPS allows for the identification of the chemical species present in the GDL after grafting. In Figure 4.8, a comparison between a non-grafted hydrophobic GDL, and GDLs grafted with NVF and AA, respectively, is presented. The general survey acquired on the untreated sample shows the presence of two main peaks (F1s at a binding energy of around ~690 eV and C1s at ~285 eV) originating from the FEP coating and GDL carbon fibers, respectively, without any observable oxygen peak. After grafting the GDL with NVF two additional peaks are detected: the N1s and O1s located at a binding energy of 401 eV and 533 eV, respectively, which originated from the grafted NVF molecules. When grafting with AA and with posterior Na replacement, the Na1s and O1s peaks are detected at 1073.5 eV and 532.5 eV. The XPS surveys verify the presence of the grafted molecules on the surface of the coated GDL, and confirmed the possibility of monitoring the signal evolution of the GDL and of the FEP coating in parallel with the grafted molecules.

The C1s core level (region from 280 to 302 eV) is plotted in Figure 4.8.b. An analysis of the non-grafted GDL allows for the identification of three major photoemission components: (I) the C-C bonds (284.5 eV), which originate from the carbon fibers composing the GDL; (II) the signal from oxidized carbon species at around 286 eV present on the surface due to partially oxidized carbon fibers or polymeric coating and; (III) CF\textsubscript{X} bonds located at 292.8 eV originate from the FEP coating (C-F\textsubscript{2} and C-F\textsubscript{3} respectively). The broadening and asymmetry of the CF\textsubscript{X} component and its shift to
higher binding energies is related to a local charging effect of FEP due to its non-conducting nature.

**Figure 4.8** - XPS spectra of three different samples: non-grafted Toray 30%FEP, Toray 30%FEP-g-NVF and 30%FEP-g-pAA-Na⁺. **a**: general survey spectra; **b**: C1s core level details.

The C1s peak measured on Toray 30%FEP-g-pNVF shows an increased C-C component relative to the CFₓ position, which is most probably related to a reduction in the coated FEP thickness or due to “cracking” of the polymer, leaving a higher fraction of carbon fibers exposed. Moreover, we observe the appearance of significant adjacent components at approximately 286.3 and 289.1 eV. The first probably includes representative CH₂/CH and are related to the polymer backbone. The second most probably includes the overlapping of the C=O and C-N components present in the formamide grafted molecules. C1s peaks from the Toray 30%FEP-g-pAA spectrum presents similar features, but with a much stronger increase of the C-C component. At 286.4 eV, the component from CH₂/CH is attributed to the grafted polymer backbone and a clearly distinguishable O-C=O component appears at 290 eV.

In order to quantify the grafting kinetics, XPS spectra were recorded on samples treated for different times. These measurements performed on Toray 30%FEP-g-pAA showed two interesting trends. The integration of the Na1s peak intensity permitted tracing the
grafting kinetics (Figure 4.9). The higher the amount of acrylic acid groups, the more protonic positions are available for Na\(^{+}\) exchange. The continuous increase as a function of time confirms the behavior measured with EDX and also the gravimetric characterization of FEP films. Additionally, the electrical conductivity of the material seems to increase in line with the reaction time (Appendix B, Figure 4.16).

![Graph showing grafting kinetics of Toray 30%FEP-g-pAA with Na\(^{+}\) exchange measured with XPS. The intensity of Na1s (integrated peak) is plotted versus reaction time.](image)

**Figure 4.9** - Grafting kinetics of Toray 30%FEP-g-pAA with Na\(^{+}\) exchange measured with XPS. The intensity of Na1s (integrated peak) is plotted versus reaction time.

When considering industrial implementation of this approach, a reaction under vacuum to wet the inner pores would imply the use of batch processes and higher energetic costs. For that reason, we explored alternatives for a more practical implementation. Table 4.4 shows three different grafting strategies tested with the Toray 30%FEP-g-pAA system: the use of vacuum, low surface tension solvents (such as hexane) and the addition of surfactants to increase the wettability. A measure of the degree of grafting was taken by measuring EDX spectra. The oxygen signal (from the acrylate group) was normalized to fluorine (from the coating) and showed that the use of hexane happens to decrease significantly the degree of grafting compared to use of water as solvent. This effect was also confirmed with other organic solvents such ethanol, dioxane and isopropanol (Appendix B, Figure 4.17). The addition of Triton X-100 surfactant allowed having almost a double O/F value compared to the use of vacuum, which shows its potential to be used in a continuous grafting process at atmospheric pressure. The final row in table 4.4 shows the O/F ratio of a sample which was exposed to AA solution but not previously irradiated. This measurement provides a baseline value to account for the initially present oxide groups, the residual unreacted AA and the noise of the O signal from the EDX device. For the GDLs grafted with NVF such alternative application strategies are not necessary, as the grafting solution readily wets the hydrophobic GDLs.
Tuning the wettability – from flat to porous systems

Table 4.4 - Different grafting strategies carried out in GDLs and corresponding O/F ratio extracted from quantified EDX spectra.

<table>
<thead>
<tr>
<th>Grafting strategy</th>
<th>Conditions</th>
<th>((O/F)_{\text{EDX}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum</td>
<td>15% wt. AA (H(_2)O), 50 mbar, 60°C, 60 min, 50 kGy</td>
<td>0.25</td>
</tr>
<tr>
<td>Low (\gamma) solvent</td>
<td>50% wt. AA (hexane), 1 atm, 60°C, 60 min, 50 kGy</td>
<td>0.053</td>
</tr>
<tr>
<td>Surfactant</td>
<td>15% wt. AA (H(_2)O) + 1.2 mL/mL Triton X100, 1 atm, 60°C, 60 min, 50 kGy</td>
<td>0.59</td>
</tr>
<tr>
<td>Contaminated</td>
<td>15% wt. AA (H(_2)O), 50 mbar, 60°C, 60 min, 0 kGy</td>
<td>0.034</td>
</tr>
</tbody>
</table>

4.4.3 Grafted GDLs: wettability

As described in the introduction, the relation between the intrinsic GDL contact angle and the observed external contact angle is not straightforward mainly due to the roughness and heterogeneity of the material. Droplets on top of rough surfaces define so called apparent contact angle (\(\theta_{\text{app}}\)), which is a function of the wettability of the material, i.e. its intrinsic contact angle (\(\theta_{\text{int}}\)) and of the geometrical properties.

In order to quantify the wettability of modified GDLs, external contact angles (\(\theta_{\text{app}}\)) were measured. The effect of reaction time using equally coated substrate (Toray 30% wt. FEP) is plotted for both grafting systems (Figure 4.10.a). The apparent contact angle (\(\theta_{\text{app}}\)) measured for the untreated substrate is around 137°. For the Toray FEP-g-pAA samples, the apparent contact angle decreases already to values around 125° after reacting for merely 5 and 15 minutes. Higher reaction times provide \(\theta_{\text{app}}\) on the order of 100-110°. However, with 30% wt. FEP coating load, it is not possible to produce a spontaneously imbibing Toray surface. When considering the FEP-g-pNVF system, much lower contact angles were measured. After only 5 minutes of grafting, the surface remains hydrophobic (\(\theta_{\text{app}}\approx 110°\)), yet after 15 minutes the surface appears hydrophilic (\(\theta_{\text{app}}\approx 50°\), even though the droplet still remains on the surface). Higher reaction times produce surfaces that spontaneously wick water droplets into the porous medium. Therefore, the \(\theta_{\text{app}}\) measured after short times (less than 2 seconds) can be considered to be 0°. It is worth mentioning that pristine samples (Toray 30%FEP non-irradiated) which have been deliberately contaminated with monomer solutions (exposed to the NVF or AA solutions at the same temperature for 120 minutes) do not show a
significant variation of their wetting properties. The fact that $\theta_{\text{app}}$ does not change (and therefore remains hydrophobic) indicates that, as desired, the grafting process occurs if the material has been previously activated by ionizing radiation. This shows the possibility of performing local modification in GDL materials, as the regions exposed to radiation can easily be defined with the help of blocking masks.

![Figure 4.10](image)

**Figure 4.10** - Apparent contact angles measured on differently treated GDLs. **a**: Effect of reaction time at a coating load of 30 % FEP. **b**: Effect of coating load at a reaction time of 60 min. The “NVF contaminated” and “AA contaminated” refer to measurements on samples which have been artificially exposed to monomer solutions.

In figure 4.10b, the $\theta_{\text{app}}$ is plotted against the FEP coating load in the GDLs at a fixed reaction time. Uncoated GDLs hold a water droplet with a CA of around 107°, even though the internal wettability of carbon fibers is around 80°. This clearly shows the influence of roughness on the apparent increase of contact angle. For the lower coating loads (5, 15 and 30% wt. FEP) the pAA treated GDL still remains hydrophobic. Interestingly, for higher coating loads (50 and 70 % wt. FEP) the surface becomes hydrophilic and spontaneously absorbs the water droplets. This dynamic process happens much slower than in the case of the NVF treated samples (it takes longer than 2 minutes to imbibe the complete water volume in the GDL). The FEP-g-pNVF system shows a quite different behavior. At 5 % wt. FEP load, the surface is already apparently hydrophilic (around 78°), however droplets still sit on the surface. At higher coating loads (15% wt. FEP and above) the surface becomes hydrophilic and spontaneously imbibes every droplet on the surface.
Unfortunately, the internal contact angles were not accessed experimentally. Some methods to quantify them have been reported, such as environmental scanning electron microscopy (ESEM) and the measurement of imbibition dynamics (Washburn)\(^84, 86, 90\). However, these characterization techniques require long experimental times and the interpretation of results is not straightforward. For that reason, we decided to estimate averaged internal contact angles derived from our measurements in flat surfaces, where Young’s equation applies.

We assume that the contact angle of the carbon fibers \((\theta_{\text{int}}^{\text{cf}})\) is 80°\(^137\). The average internal contact angle is estimated as:

\[
\theta_{\text{int}} = \theta_{\text{int}}^{\text{FEP-g-i}} f_c + \theta_{\text{int}}^{\text{cf}} (1 - f_c)
\]

where \(f_c\) is the fraction of the total carbon fiber surface covered by the coating (which is subsequently grafted). \(f_c\) was estimated to vary with the coating load (from 0 to 70% FEP) linearly between 0 and 1 (total coverage). The internal contact angle of the grafted coating, \(\theta_{\text{int}}^{\text{FEP-g-i}}\), was extracted from the experimental values obtained in FEP modified films (Figure 4) as function of reaction time and amount of grafted copolymer (FEP-g-pAA or FEP-g-pNVF).

![Figure 4.11 - Relation of estimated internal contact angles with their apparent contact angle measured on GDLs (left). Calculation of the stability regions considering Cassie-Baxter and Wenzel theories (right).](image)

It is expected that some error is induced by this simplified approach to calculate the internal contact angle, since the coating coverage fraction is difficult to estimate and the cylindrical shape of the fibers influences the internal wettability as well. However, it is rather acceptable to define \(\theta_{\text{int}}\) domains: the “FEP domain” delimited by the intrinsic contact angles of carbon fibers and FEP coating. The higher the coating coverage, the
closer the average value will tend towards $\theta_{\text{int}}^{\text{FEP}}$. The “AA domain” is limited by the wettability of carbon fibers and the minimum achievable contact angle with the FEP-g-pAA system, around 50°. Finally, the “NVF domain” is limited by $\theta_{\text{int}}^{\text{cf}}$ and $\theta_{\text{int}}^{\text{NVF}}$ (around 20°). As can be seen in Figure 4.11, many of the measured samples are beyond the regions defined by the Wenzel theory: intrinsically hydrophilic materials hold droplets with apparent contact angles higher than 90°. Such a behavior is explained by the Cassie-Baxter theory \[31\], which assumes that air (or air partially saturated with the liquid vapors) can remain trapped in the surface asperities.

As can be seen, the Cassie-Baxter theory covers the region of our experimental observations well. It demonstrates the possibility of having metastable hydrophobic surfaces, even though the material is intrinsically hydrophilic.

**Figure 4.12** - Wetting dynamics measurement. The absorbed volume normalized with respect to the initial volume is represented versus time for three Toray GDLs, coated with different FEP loads (15, 30 and 70 %wt. FEP) and reacted under the very same conditions (pure NVF at 70°C during 60 minutes).
Interestingly, the coating load has a considerable influence on the wetting dynamics. As can be seen in Figure 4.12, the material coated with 15% wt. FEP happens to have the slowest absorption dynamics, having around 50% of the droplet volume absorbed after 1 second. Increasing coating loads directly translate into faster imbibition dynamics. After 0.3 seconds a 50% droplet volume has been absorbed (30% wt. FEP) and only after 0.1 seconds the same volume has been absorbed at the highest coating load (70% wt. FEP). Increasing the coating load leads to a higher fraction of carbon fibers covered and therefore different average intrinsic contact angle.

4.4.4 Thermal degradation

As explain in the “Methodology” section, the posterior application of an MPL would expose the modified materials to elevated temperatures. Therefore, the effect of these thermal stresses on the modified polymer films is evaluated in this section. This study on thermal degradation starts with the presentation of the TGA response.

Figure 4.13 - TGA analysis performed on both grafting systems using FEP films as substrate. a: Comparison between FEP, FEP-g-pAA and FEP-g-pAA-\( \text{Na}^+ \); b: Comparison between FEP, FEP-g-pNVF, FEP-g-pVAm and FEP-g-pVAm-Cl.

Figure 4.13 presents a comparison of the FEP-g-pAA and FEP-g-pNVF systems. When comparing the FEP base material with the FEP-g-pAA, a notable mass loss is observed starting at 200-250°C (Figure 4.13.a). Interestingly, the sodium acrylate salt significantly
protects the material from thermal degradation. Much less degradation happens in the low temperature range and bulk degradation starts after 400°C.

When analyzing the FEP-g-pNVF (Figure 4.13.b), an initial mass loss of around 20% is measured after 270°C (very close to the melting temperature of the polymer), followed by a more drastic loss at around 500°C, probably related to the ultimate thermal decomposition. The formation of the amine (FEP-g-pVAm) happens to induce a pronounced degradation at even lower temperatures (starting at 100-150°C). The formation of the quaternary chloride salt (FEP-g-pVAm-Cl) provides the material with a thermogravimetric footprint very similar to that of FEP-g-pNVF.

![Figure 4.14](image)

Figure 4.14 - Transmission FTIR spectra of samples exposed to different thermal conditions (pristine, after 2 hours at 100°C, after 15 minutes at 270°C and after 2 hours at 270°C); **a**: FEP-g-pAA; **b**: FEP-g-pNVF.

The FTIR spectra acquired with thermally degraded samples show significant chemical changes. After exposing the FEP-g-pAA to 270°C (Figure 4.14.a), the region between 1510 and 1890 cm\(^{-1}\) which is attributed to the C=O stretch vibration in carboxylic acids, switches from one band in the pristine sample (1724 cm\(^{-1}\)) to two bands (1604 and 1730 cm\(^{-1}\)) after the high temperature treatment. The latter two bands can be assigned to -CO-O-CO- stretching modes, and in combination with the decrease in intensity of the broad O-H stretching band from 2450 to 3710 cm\(^{-1}\), are indicative of acetic anhydride formation in the grafted polymers. This effect is significantly enhanced by longer treatment times. In contrast, the spectra obtained for FEP-g-PAA-Na\(^+\) (Appendix B, Figure 4.18) show no evidence of chemical degradation due to the thermal treatment, i.e., the C=O stretching bands at 1410 cm\(^{-1}\) and 1570 cm\(^{-1}\) are comparable in all cases. This supports our expectation that the sodium salt impedes anhydride formation. A comparison of the pristine film with the mild condition treatment (100°C during 2 hours) shows no clear evidence of changes in chemical bonding. McNeill et al.
proposed a reaction mechanism based on intramolecular dehydration which leads to the formation of six-membered glutamic anhydride rings[140]. The same authors demonstrated as well the superior thermal resistance of the sodium salt due to absence of anhydride formation.

For FEP-g-pNVF (Figure 4.14.b) there is no clear indication of degradation at low temperature. Substantial degradation only takes place at 270°C. Most bands related to the secondary amide in FEP-g-NVF decrease in intensity or shift due to thermal treatment. The band between 1490 and 1790 cm⁻¹ linked to the –NH₂ scissoring band, the absence of the band at 1442 cm⁻¹ and the lower intensity of the broad band between 2810 and 3690 cm⁻¹ are indicative of amine formation and probably a partial loss of functionalization. Otherwise, no significant differences are observed between the spectra of FEP-g-pNVF at different degradation times (at 270°C).

![Figure 4.15 - Contact angle of water measured on films. The pristine sample represents the material after preparation but before being exposed to any degradation protocol.](image)

The observations of the chemical bond changes due to both thermal degradation protocols were subsequently correlated to the surface wettability response. The contact angle of water is represented in Figure 4.15 for differently degraded FEP films, as well as its precursor (FEP films or grafted films before any degradation protocol). The CA of pure FEP does not significantly change after any of the treatments, even after melting of the polymer. This behavior is well explained by the lack of chemical changes measured with FTIR (Appendix B, Figure 4.19).
FEP-g-pAA appears to suffer severe degradation with temperature, an effect that translates into its surface wettability. Exposure to 100°C did not significantly change its CA, however the exposure of the material to 270°C brought about a complete loss of its hydrophilic properties. Interestingly, when replacing the protons of the acrylate with Na⁺ and forming the acrylate salt, the surface wettability appears to be protected against thermal stress. Even after long treatment at 270°C, the surface is able to hold water droplets with the same CA as the initial system (∼50°). FEP-g-pNVF degrades in a similar way as FEP-g-pAA. Exposure to 100°C does not significantly change its surface CA, whereas temperatures of 270°C return the surface to the initially hydrophobic state, even after short exposures (15 minutes).

Two possibilities are proposed to mitigate these negative effects: the first includes the formation of polymer salts, such as the formation of the sodium acrylate which avoids the formation of the anhydride. The second approach would imply the use of short-time-exposure localized heat, such as infrared heating to sinter the MPL. The objective is to minimize the heat arriving to the GDL layer which would render to temperature increases and damage of the grafted coating. Some patented technologies already mentioned the use of infrared heating to apply MPLs.[141]

4.5 Conclusions

We demonstrated that the wettability of fuel cell GDL materials can be effectively tuned using radiation grafting. The key findings of this paper are the following:

- It is possible to perform surface grafting induced by a penetrating radiation – a prerequisite for the contact angle modification of porous materials such as fuel cell GDLs. Notable differences in this respect between acrylic acid, which tends to graft in the bulk of polymer, and N-vinylformamide, which tends to graft on the surface, were identified by a combination of property changes (weight increase and contact angle) and FTIR analysis.

- The grafting parameters identified using polymer films could be transferred to the grafting on the polymer coating inside fuel cell GDLs, with similar reaction kinetics. Although gravimetric measurements and FTIR are not applicable in this case, the extent of grafting and the chemistry of grafted components could be confirmed using elemental analysis (by SEM-EDX) and XPS.

- The discrepancy (known for hydrophobic GDLs) between the contact angle measured externally and the intrinsic contact angle of the polymer has important implications for the characterization: even certain materials known to have a hydrophilic internal contact angle after our treatment were apparently
hydrophobic in sessile drop measurements. This apparent contradiction was explained in light of the Cassie-Baxter theory.

- For a given set of grafting parameters, the coating load was observed to have a significant impact on the wetting characteristics: the higher the coating load, the more hydrophilic the material. This result suggests that lower coating loads leave a fraction of the carbon fiber surface uncoated.

- In view of applying an MPL including a sintering step at relatively high temperature, studies were conducted to evaluate the ability of the material to withstand these temperatures. Exposure to a temperature of 270°C (the sintering temperature of FEP) was shown to severely degrade the grafted components. However, results from thermogravimetric analysis show that the onset of thermal degradation is at 200-250°C and that alternative MPL sintering strategies such as local heating using infrared would probably avoid it.
4.6 Appendix A – Calculation of apparent wettability

Historically, two main theories are used to explain the deviations of contact angle when considering rough surfaces or porous materials: Wenzel and Cassie-Baxter. The Wenzel theory, also referred to as homogeneous wetting regime, assumes that the liquid is in contact with the solid interface\[30\]. Intrinsically hydrophilic materials present lower apparent contact angles while internally hydrophobic materials hold higher apparent contact angles. The roughness factor, \( r_f \), defined as the ratio between the developed surface area of the material and its geometrical area, relates the intrinsic and apparent contact angles to each other:

\[
\cos \theta_{\text{app}} = r_f \cos \theta_{\text{int}} \tag{4.4}
\]

As can be seen in Figure 11, many of the measured samples are beyond the regions defined by the Wenzel theory: intrinsically hydrophilic materials hold droplets with apparent contact angles higher than 90°. Such a behavior is explained by the Cassie-Baxter theory\[31\], which assumes that air (or air partially saturated with the liquid vapors) can remain trapped in the surface asperities. The apparent contact angle can be calculated as:

\[
\cos \theta_{\text{app}} = f_1 \cos \theta_{\text{int}} - f_2 \tag{4.5}
\]

Where \( f_1 \) is the total surface of solid-liquid interface and \( f_2 \) is the total surface of air-liquid interface. Following the original treatment performed by the authors, a highly simplified model assumed that our texture is composed of a variety of parallel cylindrical fibers, with a fiber radius \( r \) and a distance between two fiber centers defined as \( 2(r+d) \). Using geometrical relations, the values for \( f_1 \) and \( f_2 \) can be calculated as:

\[
f_1 = \frac{\pi r}{r+d} \left(1 - \frac{\theta_{\text{int}}}{180}\right) \tag{4.6}
\]

\[
f_2 = 1 - \frac{r \sin \theta_{\text{int}}}{r+d} \tag{4.7}
\]

This expressions permit calculating apparent contact angles as function of their intrinsic ones, considering the geometry and intrinsic wettability. Due to the complexity of the GDL microstructure, different values of \((r+d)/r\) were plotted in figure 4.11.
4.7 Appendix B – Supplementary material

4.7.1 Local Charge effect measured with XPS: increase of conductivity with grafting degree

Even if an electron flood gun was used, the charge effect could not be completely compensated. However, an interesting decrease in charge was systematically measured at increasing reaction times with the Toray FEP-g-pAA system. The higher the grafting degree, the lower the charge effect due to higher symmetry of the CF\textsubscript{X} component (Figure 4.16). Therefore, we could assume that the copolymer FEP-g-pAA is more electrically conducting than neat FEP.

The increase in electrical conductivity of the samples can only be affected by two main reasons: the cracking of the polymer which facilitates electron conduction and the structural change of the original FEP coating, which has very low electric conductivity. A significant decrease of specific electric resistance (more than two orders of magnitude) was reported in the literature when grafting polymer films of PTFE and FEP with acrylic acid\cite{130, 131}.

Figure 4.16 - XPS spectra of Toray 30%FEP-g-pAA grafted at different reaction times. The increased of symmetry of the C-F\textsubscript{x} peaks indicates reduction of charge effect.
4.7.2 Effect of solvent replacement in grafting solution

Fluoroethylene propylene (FEP) and polytetrafluoroethylene propylene (PTFE) were reacted with acrylic acid to form FEP-g-pAA and PTFE-g-pAA, respectively. In this case, the monomer solvent was a mixture of water with isopropanol, dioxane or ethanol. As shown in Figure 4.17 the degree of grafting (DG) was significantly decreased when increasing solvent concentration, which justifies our decision to use water as solvent.

![Figure 4.17 - DG over percentage of solvent in water for FEP-g-pAA (left) and PTFE-g-pAA (right).](image)

4.7.3 Thermal degradation on FEP-g-pAA-Na⁺

![Figure 4.18 - FTIR (transmission mode) spectra of differently degraded FEP-g-pAA films, showing no significant changes. Particularly, no anhydride formation is detected.](image)
4.7.4 **Thermal and chemical degradation on pristine FEP films**

![FTIR-ATR spectra on differently treated FEP pristine films](image)

**Figure 4.19** - FTIR-ATR spectra on differently treated FEP pristine films, showing no significant variation due to thermal or chemical stress. Chemical degradation refers to exposing the FEP films to Fenton’s reagent (30%vol. H₂O₂, 30 ppm Fe²⁺, 80°C) during 8 hours. Ageing refers to FEP films which were stored under air for long periods of time (more than a year).
Chapter 5. Mask-assisted electron radiation grafting

While in the previous chapter a detailed study on synthetic conditions to modify samples homogeneously, the present chapter focuses on the translation to patterned structures. To do so, we used mask-assisted electron radiation grafting. In particular, the influence of electron energy on the achieved spatial resolution is discussed. The present chapter contains a combination of experiments and numerical simulations. The experiments were performed by irradiation FEP films and GDLs with different mask designs and setups and the Monte Carlo simulations using the PENELOPE code. In the final part of this chapter, the influence of the spacing between mask and sample and the impact of backscattering are also investigated.

The present chapter consists of a reproduction of the following publication:
5.1 Abstract

The spatial resolution aspects of the local modification of porous materials by electron induced graft-polymerization were studied by a combination of experiments and numerical simulations. Using blocking masks, only selected regions of the material were exposed to radiation and subsequently grafted. The main focus of this study is the application to gas diffusion layers, a carbonaceous 200 μm thick porous substrate widely used in fuel cells, with the goal of improving water management by locally tuning the wettabillity. The comparison of experiments performed with different electron energies and corresponding simulations shows good agreement, identifying the energy threshold necessary to graft through the material to be approximately 150 keV. The impact of electron energy on spatial resolution was studied, showing that the blurring effects due to electron scattering reach a maximum at around 200 keV and are reduced at higher electron energies. Finally, the numerical simulations were used to define the conditions necessary to selectively graft only parts of bi-layer fuel cell materials.

5.2 Introduction

In the last 70 years, the use of electron beam technologies has impacted various fields, such as micro and nanofabrication[142-145], electron microscopy, curing[146-148] and welding[149], among others. Electron-beam lithography (EBL) is a technique based on the use of a focused electron beam to draw custom shapes into so-called resist layers, i.e. an electron-sensitive material, which undergoes either chain scission (polymethyl methacrylate (PMMA)) or cross-linking (e.g. SU-8) upon electron exposure and allows for pattern definition by selective removal of the irradiated (or non-exposed) fraction of the resist upon development. EBL is nowadays used in a number of applications and has been developed over the years to manufacture sub 10 nm resolution structures[150, 151]. Due to the demanding technology required to focus the beam, EBL is a very costly technique (> 2 M$/device[150]). There are, however, other applications that do not require such narrow structures. There have been recent works, mainly in the field of microfluidics, focusing on the production of patterns on a scale of tens to hundreds of micrometers using different technologies, such as plasma[152], UV irradiation[117], among others. To the best of our knowledge, none of these studies have focused on modifications of thick porous materials (thickness > 100 μm) using electron beams, which we address in this work.

Our group has recently developed a method to modify porous gas diffusion layers (GDLs) used in polymer electrolyte fuel cells (PEFCs)[28, 153]. The method is based on electron radiation grafting of the polymeric coating covering the carbon fibers [23, 24].
The grafting polymerization refers to the formation of a copolymer between the original polymer (pA) and a newly added monomer (M)\cite{13, 129, 154}. The resulting molecular structure can be written as pA-g-pM. Normally, pA is a low cost structural polymer and M introduces an additional valuable property. In our particular case, pA is a hydrophobic polymer (fluorinated ethylene propylene copolymer (FEP)) and M is a hydrophilic compound (here acrylic acid) to increase the wettability. Since the minimum expected pattern width to be produced is in the range of 100 \( \mu \)m, we use masks to block the radiation in the undesired regions. By adequately selecting the electron energy the beam should penetrate the entire material thickness, generating radicals in the polymeric coating located under the mask-free regions. In a subsequent step, the activated materials are brought in contact with a liquid solution containing the hydrophilic monomer and the grafting polymerization starts on the activated regions. The control of the experimental conditions (type of monomer, concentration, solvent, temperature, reaction time, etc.) allows for tuning the desired final properties\cite{155}.

![Illustration of the synthetic process to obtain porous substrates with structured properties.](image)

**Figure 5.1** - Illustration of the synthetic process to obtain porous substrates with structured properties. (a) electron radiation using a blocking mask; (b) activated material is brought into monomer solution; (c) finally, a material with localized grafted regions is obtained.

While a number of fields could benefit from the work on modifying thick porous substrates, the implementation of GDLs with patterned wettability in PEFCs is expected to improve the complex water management by providing optimized liquid/gas transport characteristics\cite{156}. We have demonstrated significant fuel cell performance increase when using the novel GDLs using the mask-assisted radiation grafting method\cite{74, 157, 158}. The objective of this paper is to provide a more fundamental understanding on how the radiation dose is distributed and, from this knowledge, set the guidelines to produce a second generation of GDLs with patterned wettability with higher resolution and tailored penetration depth.
We start by comparing experimental results of elemental analysis on top and bottom surfaces with Monte Carlo simulations of electron transport in a reproduced geometry. In these lines, we compare the achieved resolution as a function of the electron energy and discuss the 2-dimensional dose distribution. Afterwards, the effect of separating the mask and the substrate is studied experimentally for different distances. Simulations provide a theoretical basis of the forward scattering phenomena at two energies. Further, we theoretically explored the impact of backscattering by using different materials on the back-side of the substrates. The paper closes by presenting an example of the use of simulations in a predictive way by irradiating a bi-layer material to a pre-selected penetration depth.

5.3 Experimental methods and simulations

The experiments are used to quantify the distribution of grafted molecules on top and bottom surfaces, and the simulations to calculate the absorbed dose distribution through the thickness of the material as well as to extrapolate the results to ranges of energies not accessible with the currently used electron sources. The experimental methodology consists of the following steps: (I) GDLs are electron beam irradiated using masks; (II) activated GDLs react with the monomer, acrylic acid; (III) grafted GDLs are cleaned and exposed to sodium hydroxide (NaOH) in order to replace the protons in the acid groups by a sodium ion (Na\(^+\)) for visualization purposes; (IV) elemental mappings are recorded using energy dispersive X-ray analysis; (V) elemental mappings are processed and profiles of the grafting yield are obtained. The following subsections introduce the materials, procedures and techniques used, alongside with details of the Monte Carlo simulations.

5.3.1 Materials

5.3.1.1 Masks

2 mm thick stainless steel masks were used. Rectangular openings were machined using a pressurized water jet (WATERjet, Aarwangen, Switzerland). Two types of masks were used for the studies reported herein: (1) a mask containing rectangular slits of 0.5 mm width spaced 5 mm; (2) a mask with two perpendicular rectangular slits (500 µm width) forming a cross-like shape. The first mask was used for the studies about penetration depth and resolution, while the second mask was used for the beam broadening study to elucidate beam divergences in different spatial directions. The slits of mask (I) were placed in the direction parallel to the linear electron beam axis.
5.3.1.2 Gas diffusion layers (GDLs)
Untreated Toray Paper 060 (TGP-H-060) was used as base GDL material (purchased at Fuel Cell Earth Store). It has a thickness of ~200 μm, a bulk density of 0.44 g cm\(^{-3}\) and a porosity of ~78%. The material was coated with FEP using the “dipping” method followed by a thermal treatment. The details about the coating application were described elsewhere\[155\]. For this particular study, a coating load of 70% (weight of the coating relative to the base material) was used. We decided to use a high coating load to have a sufficient amount of polymer to perform elemental mappings with a good image quality.

5.3.1.3 FEP films (as dosimeters)
Fluorinated ethylene propylene (FEP) films of 25 μm thickness were used (DuPont\textsuperscript{TM} Teflon\textsuperscript{®} FEP Gauge 100) for measuring the beam width in the beam broadening study (Section 3.3). The foils were cut into pieces of 6 cm x 6 cm and rinsed with abundant ethanol to remove any contaminant present. Afterwards, they were dried at 60°C in vacuum overnight before being packed into bags.

5.3.2 Electron beam
Two electron beam installations covering different energy ranges were used:
1) A linear accelerator was used at LEONI Studer (Däniken, Switzerland) with a variable accelerator energy range of 1.05-2.35 MeV, a beam intensity range of 0-35 mA and a scan width of 1220 mm. Materials are mounted on metallic trays that are conveyed through the irradiation facility. Tray speed [m/min] and current beam [mA] are adjusted to control the dose. 1 cm thick polyethylene (PE) was placed between the metallic tray and samples in order to reduce the backscattering. Unless otherwise stated, a fixed electron energy of 2.1 MeV was used, the other two parameters being variable to achieve the desired dose.

2). Low-energy electron beam treatment was carried out in an EBLab 200 sealed laboratory emitter system from Comet AG (Flamatt, Switzerland). Samples were subjected to different doses ranging from 50 kGy under nitrogen (<200 ppm oxygen), employing an acceleration voltage between 80 and 200 kV and a maximum dose of 50 kGy per pass at a transport speed of 12 m/min and a nominal air gap of 10 mm.

Samples and masks were placed on a frame-type holder. This holder was gas sealed by covering the upper part with a 30 μm thick polyethylene terephthalate (PET) film and a combination of O-rings and screws. The sealing of the holder was done to avoid any decomposition products potentially produced during irradiation to damage the
5.3.3 Grafting reaction

Polyacrylic acid (pAA) was chosen as grafting system due to the favorable kinetics and easiness to characterize. Acrylic acid (Sigma Aldrich 99% containing 180-200 ppm MEHQ ad inhibitor) was used as received. The monomer was diluted in water down to 15% by weight. Extensive work was performed to find synthetic conditions allowing a straightforward quantification of the grafting (i.e. a significant amount of acrylic groups leads to color changes and sufficient molecules for the elemental mapping). On the contrary, elevated grafting degrees are known to produce significant expansions of sample size with the FEP-g-pAA system. Since the paper discusses localized modifications, we have chosen the conditions resulting in minor size expansion allowing for measureable quantification.

Activated GDLs and FEP films were placed in cylindrical glass reactors (volume around 70 mL) together with the grafting solution at atmospheric pressure. In order to de-oxygenate the media, nitrogen flushing of the solution was performed during 60 minutes. Afterwards, the reactors were placed in a controlled temperature water bath at 60°C for 30 min. Samples were cleaned using a vacuum filter system with ethanol, isopropanol and water. Finally, they were dried under vacuum at 60°C before further preparation for characterization purposes.

5.3.4 Characterization

The replacement of protons (from the acidic group) to sodium ions (Na+) to form sodium polyacrylate resulted in a significant improvement of elemental signal measured with energy-dispersive X-ray analysis (EDX). To do so, samples were punched (6 mm diameter) and immersed into a 0.025 M NaOH solution (solvent composed of 60%wt. H2O and 40%wt. EtOH) and stirred overnight. After that, they were rinsed with water to remove excess salt and dried under vacuum.

EDX elemental mapping was chosen for the characterization of the patterns. An FE-SEM Ultra 55 (Carl Zeiss, Oberkochen, Germany) with a compatible accessory (EDAX TSL, AMETEK) was used. Elemental mappings were obtained for carbon, fluorine, oxygen and sodium (Figure 2) on the external surfaces of the modified GDL. In this work we refer to “top” as the surface facing the electron beam and “bottom” the opposite surface. The carbon signal comes from carbon fibers and coating (to a lesser extent), while fluorine is exclusively present in the polymeric coating (FEP). Sodium
should be exclusively present in the sodium polyacrylic acid molecules, while oxygen comes mainly from the grafted co-polymer and some partially oxidized carbon fibers and FEP. That is the reason why we chose sodium to perform further analysis. It should be emphasized the fact that even if we refer to external surfaces, the EDX does not prove the very external surfaces (like X-ray photoelectron spectroscopy does, for example); however the X-rays are emitted from some deeper locations of the material (i.e. 0.5-2 μm). This effect is shown as “excitation pear”. On top of that, the porous and rough nature of the GDL also increases the probability to probe some material layers located underneath. As an arbitrary value, we consider 30 μm as the external surfaces within this work.

As shown in Figure 5.2, we calculated the ratio between Na and F signals. Since the coating content and distribution is not the same for each sample, this normalization permits obtaining more reliable results. As the Na/F ratio as a measure of the amount of grafted polymer only makes sense in locations where the coating is present, a threshold was set on the fluorine (F) signal below which the Na/F ratio was defined as “unknown”. The values in these regions were obtained from the adjacent regions using

Figure 5.2 - The original EDX mappings for C, F and Na are shown on the top. Processed mappings containing Na/F, interpolated Na/F and a combination of Na/F with C are shown on the bottom. The mappings correspond to a 500 μm pattern using 180 keV (on the top surface).
linear interpolation. Following this, a “final image” was created by overlaying the signals from the fibers (C), the coating (F) and the grafted polymer (Na/F).

For the measurements of beam broadening using flat FEP films, we used optical microscopy (Leica VZ700 C) and relied on opacity evolution in the modified areas. The originally transparent FEP film becomes opaque in the regions where a significant amount of polyacrylic acid has been grafted (FEP-g-pAA). It must be noted that very small grafting degrees may not lead to visually identifiable loss of transparency. For this reason, the results obtained with this method are semi-quantitative.

5.3.5 Simulations

5.3.5.1 Environment

The code system PENELOPE (Penetration and Energy Loss of Positrons and Electrons) was used for performing the simulations presented in this paper (version 2015)[105-107, 159]. PENELOPE performs Monte Carlo simulations of coupled electron-photon transport in arbitrary materials for a wide energy range (50 eV – 1 GeV). The code system contains state-of-the-art physics for particle transport. We prepared scripts to simulate the various geometries and source characteristics described in the respective chapters. If not otherwise stated, $10^7$ electrons were used for each of the simulations.

5.3.5.2 Geometry definition

In order to represent the studied system, a geometry space was defined as shown in Figure 5.3. Generally speaking, it consists of a stack of horizontal planes which are infinite in the $y$ direction (perpendicular to the paper) and infinitively long in the $x$ direction. The electron beam source has been placed above the Body I at a distance of 10 mm. We have considered mono-directional beam flux as a good representation of the experimental situation where a frame moves and gets irradiated using a linear source. We considered the source to be sufficiently long in $x$ and $y$ direction and 5 mm in $z$ direction. Body I corresponds to a layer of PET, used to seal the irradiation frame (as described in 2.2). This layer is ~30 µm thick and has been included in the simulations. Body II corresponds to the steel mask. It is 2 mm thick and has a slit opening of 0.5 mm. Body III represents the material of interest (GDL) and is 200 µm thick. Normally, the distance between the mask and the GDL ($D_{ms}$) is 0 µm, except in the study about the impact of mask-GDL distance (Section 3.3). Body IV is only considered in some cases and can refer to an additional layer with different properties (such as microporous layer) or to a material underneath to modify the backscattering. In the case that an MPL is considered, the distance between Body III and Body IV ($D_{sb}$) is 0 µm, however two distances were used (0 and 200 µm) when a backscattering material was considered.
5.3.5.3 Material properties

Table 5.1 contains a collection of the materials used in this work and the most relevant properties. Some materials were already included in the PENELOPE database and therefore no elemental composition needed to be input.

<table>
<thead>
<tr>
<th>Name</th>
<th>Thickness [µm]</th>
<th>Density [g cm(^{-3})]</th>
<th>Composition %wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET (Body I)</td>
<td>0.03</td>
<td>1.40</td>
<td>-</td>
</tr>
<tr>
<td>Steel (Body II)</td>
<td>2.0</td>
<td>7.90</td>
<td>17(Cr), 12(Ni), 81(Fe)</td>
</tr>
<tr>
<td>GDL (Body III)</td>
<td>0.2</td>
<td>0.75 (^{[160]})</td>
<td>31(F), 69(C)</td>
</tr>
<tr>
<td>FEP (Body III)</td>
<td>0.2</td>
<td>2.20</td>
<td>-</td>
</tr>
<tr>
<td>MPL (Body IV)</td>
<td>0.05</td>
<td>1.60 (^{[16]})</td>
<td>18(F), 82(C)</td>
</tr>
<tr>
<td>PE (Body IV)</td>
<td>0.10</td>
<td>0.940</td>
<td>-</td>
</tr>
</tbody>
</table>

The steel elemental composition used is obtained from a typical stainless steel 316L type as used in the experiments\(^{[161]}\). The elemental composition for GDL and MPL was calculated considering the FEP polymer content (70%wt. in the GDL and 30% in the MPL) and the material porosity (0.70 for the GDL and 0.24 in the MPL). The porous material was represented by using an apparent density computed by the contributions of solid materials and air void. Future work will include the utilization of complex geometries to capture the effect of different fiber orientations.
5.4 Results and Discussion

5.4.1 Penetration depth and resolution dependence on electron energy

The first section of results focuses on the effects of electron energy on the resolution and penetration depth. We start by showing the experimental results of the EDX mapping at varying electron energies (Figure 5.4). For every energy value, it can be clearly seen that a sharply defined pattern of around 500 μm appears on the top surface. More details on dose distribution will be discussed in Figure 5.5 and following paragraphs. Analyzing the bottom surfaces, no measurable grafted pattern was observed on samples irradiated with the lowest energies (120 and 140 keV), which indicates that electrons are not penetrating the complete material thickness, or that the dose absorbed at the bottom surface is too low to allow measurable grafting polymerization.

![Figure 5.4 - Processed EDX mappings at different electron energy values and showing the top and bottom external surfaces of the GDL. Similar to Figure 5.2, red and blue color represents F and Na/F, respectively.](image-url)
At higher energies, $E > 160$ keV, the pattern also appears at the bottom surface and has a similar width as the pattern at the top. However, the relative concentration of grafted molecules seems to be lower, which could indicate a reduced dose reaching the bottom surface or a less effective grafting processing occurring there, the second option being less probable considering the reactor design\[155\]. Interestingly, similar grafting intensity is found at the top and bottom surfaces of the modified GDL irradiated with the highest energy (2100 keV). This observation points to a more homogeneous distribution of the absorbed dose and effective grafting occurring on both sides. It should be noted that the pattern obtained at the bottom surface is slightly more blurred than the one at the top surface.

Figure 5.5 shows simulated cross-sectional 2-dimensional dose distribution images. It can be seen that maximum dose values are obtained in the center while the broadening and blurring due to scattering events appear to become significant in the energy range $E = 140$-200 keV. A region having a width of approximately 100 µm adjacent to the area where grafting is desired is thus exposed to radiation as well. The dose distribution over the x-z directions follows a conical shape, which broadens towards the bottom surface, thereby impairing the resolution at the bottom surface compared to the one at the top surface.

![Figure 5.5](image-url)

**Figure 5.5** - Simulation results of 2D dose distribution at the GDL for different values of electron energy.

Surprisingly, this effect is predicted to notably disappear when increasing the energy from 200 keV to 300 keV. In this case, the dose distribution becomes more homogeneous and scattering is significantly reduced, thereby defining higher quality
patterns. This trend persists at elevated energies and similar results are obtained in the energy range between 500-2100 keV. It should be noted that a slightly higher residual dose appears on the mask covered regions at the highest energy, $E = 2100$ keV, which could originate from secondary electrons and Bremsstrahlung transported throughout the mask.

![Graphs showing dose profiles at different energies](image)

**Figure 5.6** - Comparison of experimental and simulation results top and bottom of the GDL.

In order to assess the resolution obtained on top and bottom surfaces, we systematically calculate the Na/F intensity profiles at different energy values and display them alongside the simulation results of dose absorbed (Figure 5.6). The dose profiles were calculated considering the outer 30 $\mu$m and averaging over the $z$ direction. From experiments, it can be seen that electron radiation does not penetrate throughout the complete material at $E \leq 140$ keV (Figure 5.6.a and 5.6.b). Differences between experimental values and simulations are notable, especially in the case of 140 keV. The explanation for this could be the real PET layer thickness. If the layer would be slightly
thicker (i.e. 5-10 μm) this would significantly impact penetration depth of the porous material underneath. The definition of the porous material used in this work can also impact the results. Finally, also differences in the real air gap may have an impact despite to a lesser extent than the above.

Let us compare the experimentally obtained profiles at different energies for the top surface. A trend shows broadening of the modified regions as energy increases. The simulation results capture this trend and fairly similar pattern widths and sharpness are obtained for every value of energy. We speculate that these differences appear due to deviations of beam mono-directionality. If the electron flux does not impact the mask perpendicularly, then electrons travelling with angular trajectories have higher probabilities to be stopped by the mask side walls before reaching the GDL if they have a lower energy. This phenomenon would also justify the blurring of the edges of the modified domain, contrary to simulations that show a sharp transition. On the bottom surfaces, a broadening and blurring of the modified domain is observed as well, with a larger magnitude than for the top surface for the energies lower or equal to 180 keV (Figure 5.6.c and 5.6.d). This corresponds well to the simulation results predicting a difference in width and sharpness between the top and bottom surfaces. At the highest energy \(E = 2100\) keV, the top and bottom surface have nearly the same pattern width and sharpness, which is well represented by the simulation results. A slightly broader pattern is obtained at the bottom interface. This can be explained by backscattering originating from the holder materials underneath and will be discussed in further detail in Section 5.4.4.

It is important to stress the fact that Na/F intensity values obtained with the EDX are not linearly proportional to the dose calculated with the simulations. Several reasons contribute to such differences: (a) the relationship between dose and degree of grafting is not linear and complexly depends on monomer type, concentration, temperature, reaction time, etc.; (b) X-rays detected in EDX are not emitted only from the very external surfaces, but from a volume of some hundreds of nanometers depth (effect known as “ionization pear”); (c) the porous and heterogeneous nature of the GDL material can impair the quantitativeness of the analysis due to, for instance, incoming emitted X-rays from lower material layers. Consequently, one should bear in mind that EDX profiles at best provide a semi-quantitative description of the measurable grafting locations. In this work we do not intend to use the Monte Carlo simulations to reproduce in detail the experimental observations, but rather to provide a fundamental understanding of electron transport and energy absorbed in localized regions of thick materials. This will allow us to define irradiation strategies and design experimental setups to modify thick porous materials with improved pattern quality.
Figure 5.7 - Simulation results of absorbed dose over the z-coordinate (in the GDL) at five different energies.

The current analysis procedure does no give experimental access to the depth profile of the material modification, thus this aspect will be analyzed on the basis of simulation results. The experimental measurements on the top and bottom surfaces serve as a validation of these simulations, taking into account the slight discrepancy observed in the energy threshold necessary to penetrate through the material. Figure 7 shows the distribution of the absorbed dose over the GDL thickness according to the simulation. The maximum absorbed dose displaces to deeper z-coordinates as energy increases. Interestingly, for \( E = 300 \text{ keV} \), the dose distribution on the GDL is rather homogeneous, and there are only marginal changes when increasing this energy up to 2100 keV. The depth profile information is interesting for the practical application to fuel cells for the following reasons: (a) to define the minimum energy required in case the same properties throughout the complete material thickness are desired; (b) to pre-design modifications with selected penetration depths.

5.4.2 Influence of the spacing between mask and sample

The distance between the blocking masks and the irradiated substrate, \( D_{ms} \), has a notable influence in defining the pattern of the targeted width. Figure 5.8 shows the beam broadening as a function of \( D_{ms} \). Beam broadening, \( BB \), has been calculated as:

\[
BB = \frac{w_f - w_0}{2}
\]  

(5.1)
where $w_f$ is the final pattern width after reaction and $w_0$ is the original mask opening width (500 $\mu$m).

Figure 5.8 - Bream broadening versus mask-to-sample distance for the two spatial directions at two electron energies: (a) Illustration of the setup used and definition of directions; (b) optical micrograph showing the grafted structure; (c) 200 keV; (d) 2100 keV.
In this study, we differentiate between the direction parallel to the electron beam scanning direction, $\Delta x$, and the direction perpendicular to the beam axis, $\Delta y$ (Figure 5.8.a). At the lowest energy (Figure 5.8.b), $E = 200$ keV, it can be seen that significant broadening occurs ($\sim 2.3$ mm when the separation in 10 mm). There is a fairly good linear fit with a slope of $\sim 0.23$ mm/mm for both directions ($\Delta x$ and $\Delta y$). This could be explained by the geometry of the electron source and the position of the sample with respect to it. At higher energies (Figure 5.8.c), however, significantly different beam broadening occurs in the two directions. The broadening in the $\Delta x$ direction (slope $\sim 0.35$ mm/mm) amounts by a factor greater than two compared to that in the perpendicular direction, $\Delta y$ (slope $\sim 0.16$ mm/mm). The electron beam used at LEONI sweeps a 30° angle between the linear source and the actual sample location. It can be expected that electrons hitting the mask near the slit oriented in the $\Delta x$ direction will follow trajectories deviating from the main axis, which leads to more pronounced scattering events and loss of resolution.

![Figure 5.9 - Simulation results of beam broadening as a function of the distance between mask and sample. (a) Schematic of the configuration used for simulation; (b, c) Dose distribution over x-coordinate at (b) 200 keV and (c) 2100 keV, respectively.](image)
The experimental results previously discussed (Figure 5.8) are highly dependent on the type of electron beam (geometry, source type, dose rate, etc.) and it is therefore difficult to extract general conclusions. In order to provide a more fundamental description of the phenomena, we performed Monte Carlo simulations considering an idealized geometry as shown in Figure 5.9.a. Since we assume a mono-directional electron beam, the objective of this study is to quantify the resolution loss only due to small angle scattering events as function of the distance between a mask and the sample of interest. FEP flat thin films were used to simplify the problem as compared to thick porous materials and to reproduce the experiments. At $E = 200$ keV (Figure 5.9.b), it can be seen that very significant scattering occurs as $D_{ms}$ increases and the dose distributes over the adjacent regions. Interestingly, at $E = 2100$ keV, this effect is nearly eliminated and only slight differences exist on the dose distributed at various values of $D_{ms}$, which points to a strong influence of energy in these scattering events. For the low energies ($< 200$ keV), the effect of scattering according the simulation is in the same order of magnitude as the experimentally observed broadening. At high energy (2100 keV), the observed broadening can hardly be explained by the effect of scattering, in particular for the $\Delta x$ direction, and the observed effects are rather imputable to the angle of the electron beam, as mentioned above.

5.4.3 Backscattering as a limitation for achievable resolution

An important consideration when targeting high definition modifications on both sides of the porous material is the backscattering (i.e. large angle scattering events). In this work, we refer to backscattering as radiation that is emitted back to the body of interest after reaching some materials underneath. Depending on the used setup, these could be holders (metallic or polymeric), air or vacuum. In previous experiments of our group, we have experienced that the use of high energy electron beams (i.e. $E = 2100$ keV) combined with metallic holding trays lead to poor quality of modifications. In other words: while the directly exposed regions appeared highly activated as desired, the mask-covered areas are still significantly modified. This leads to a final material of poor quality. In our particular case, the complete material would become hydrophilic. To avoid this important issue, we tested different materials as support for the mask-GDL arrangement and found that polyethylene (PE) effectively reduced the backscattering effect and allowed the production of materials with a well-defined spatial definition of the desired modification (i.e. containing hydrophilic and unmodified hydrophobic regions). For the sake of providing some fundamental explanations to these observations, we performed simulations comparing the effects of using different
materials underneath the GDL. (Figure 5.10.a). Due to its practical relevance, the effect of the distance between the GDL and this material is also evaluated ($D_{sb}$).

![Diagram of GDL and backscattered materials](image)

**Figure 5.10** - Simulation results on backscattering. (a) Schematic of the configuration used for simulation; 2-D dose distribution using (b) steel and (c) air; Dose distribution over x-coordinate at (d) $D_{sb} = 200$ µm and (e) $D_{sb} = 0$ mm. These calculations were carried out with $10^8$ electrons and an electron energy of $E = 2100$ keV.
Very interestingly, it can be seen that the use of steel instead of PE or air leads to a significantly higher dose absorbed in the adjacent regions when using a $D_{sb} = 200$ µm (Figure 5.10.b). This effect essentially disappears when putting the GDL and the backscattering material in direct contact ($D_{sb} = 0$), which indicates that a minimum spacing is needed to facilitate the electron trajectory after the large angle scattering event. The use of PE instead of having a large space filled with air behind the sample does not result in a visible change of the dose absorbed by the GDL sample. This is consistent with the literature, as it is well known that high atomic number elements – which are absent in PE – favor the backscattering\cite{162}.

5.4.4 Application to bi-layer materials

Based on the model validation with our experimental observations, we are in a position to use the Monte Carlo simulations in a predictive way. When producing material modifications using the mask-assisted electron beam induced grafting approach, it is important to have the possibility to control the penetration depth to, for example, irradiate one layer only without imparting significant radiation to the layer underneath. State-of-the-art fuel cell diffusion layers are bi-layer materials, composed of a fibrous substrate layer (carbon paper or felt) and a so called micro-porous layer (MPL). This material, composed of carbon particles and polytetrafluoroethylene (PTFE), has a much finer porosity (~0.1 µm pore size) than the substrate and is meant to improve the contact to the catalyst as well as the water management. Depending on the design, a modification of the complete thickness or of only one of these layers – typically the substrate layer – may be desired.

Figure 5.11 - Simulation results on pre-selected penetration depth of a bi-layer arrangement GDL+MPL. (a) Schematic of the configuration used for simulation; (b) Dose distribution over $z$-coordinate at electron energies of 120, 125, 130, 135 and 140 keV; (c) 2D dose distribution at $E = 130$ keV where the $z$ direction has been stretched by a factor of 4.
In order to predict the required energy to modify only the substrate in a bilayer arrangement (Figure 5.11.a), we ran simulations (energy range between 120-140 keV) on a sample composed of two layers (each of them with their corresponding parameters, see Experimental section). As seen in Figure 5.10.b, there needs to be a trade-off between having a sufficient dose on the bottom GDL side and minimal damage on the MPL side. We selected $E = 130$ keV as the most suitable electron energy to meet these requirements and computed the 2-D dose distribution on the stack of materials.

5.5 Conclusions

A combined experimental and numerical analysis based on Monte Carlo simulations was conducted to evaluate the requirements on electron beam irradiation to perform a local modification of porous materials – in particular for fuel cells – by radiation grafting. The major findings and recommendations are:

- Electron energies larger than 140 keV are needed to modify 200 $\mu$m thick porous gas diffusion layers throughout their thickness. These results are supported by Monte Carlo simulations on electron scattering in low density carbon coated materials, though the simulation predict a slightly lower threshold energy.
- The edges of the modified regions are increasingly blurred with increasing energies until a maximum is reached at around 180-200 keV. Simulations predict that this blurring is significantly reduced again when increasing the energy to 300 keV. The experiments performed at much higher energies (2100 keV) partly confirm this trend. These results identify the energy of 300 keV as an optimal trade-off between the need of a sharp pattern and a minimal mask thickness.
- The distance between the blocking mask and the irradiated sample plays an important role. Small angle scattering events, phenomena known as forward scattering, impair the resolution significantly. Reduced energies ($E = 200$ keV) lead to significantly higher beam broadening compared to higher energies. When using lower energies, samples should be placed very near ($< 1$mm) to the blocking mask while this is substantially less relevant at higher energies – provided the beam source is arranged perpendicular to the sample in terms of electron flux direction.
- The use of low atomic number compounds at the bottom of irradiated materials reduces significantly the backscattered electrons, thereby improving the quality of the achievable spatial pattern definition. To avoid backscattering, we propose to free the bottom interface if possible for irradiation. When practical reasons due not permit so, polyethylene should be use to minimize the backscattering.
• The simulations of electron penetration depth indicate the possibility of performing a selective modification of only a selected substrate layer in state-of-the-art bi-layer fuel cell materials.
Chapter 6. Capillary pressure characterization

Once the formation of hydrophilic patterns has been described in the previous chapter, now is time to discuss how water distributes in the GDLs with patterned wettability. The present chapter focuses on \textit{ex situ} capillary pressure characterization, which consist on understanding the relationship between capillary pressure and saturation, on the modified GDLs. Neutron radiography and X-ray tomographic microscopy have been used to image the water distribution. The influence of the following material parameters has been investigated: type of carbon porous substrate, hydrophobic coating load, pattern width and grafted compound.

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6.1 Abstract

In this paper, we present an experimental study on the development of gas diffusion layer (GDL) materials for fuel cells with dedicated water removal pathways generated using radiation induced grafting of hydrophilic compounds onto the hydrophobic polymer coating. The impact of several material parameters was studied: the carbon substrate type, the coating load, the grafted chemical compound and the pattern design (width and separation of the hydrophilic pathways). The corresponding materials were characterized for their capillary pressure characteristic during water imbibition experiments, in which we also evidenced the differences between injection from a narrow distribution channel in the center of the material (and thus strongly relying on lateral transport) and homogeneous injection from one face of the material. All materials parameters were observed to have a significant influence on the water distribution. In particular, the type of substrate has a dramatic impact, with results ranging from a nearly perfect separation of water between hydrophilic and hydrophobic domains for substrates having a narrow pore size distribution to a fully random imbibition of the material for substrates having a broad pore size distribution.

6.2 Introduction

Research is striving to increase power density of polymer electrolyte fuel cells (PEFCs). Improving the catalytic activity and optimizing the water management are frequently identified as key approaches for maximizing power density or reducing the cost[125, 163-165]. The gas diffusion media (GDM), which are stacked between electrodes and flow fields, affects the complex water management in PEFCs to a significant extent. GDMs, generally composed by an arrangement of a gas diffusion layer (GDL) and a microporous layer (MPL), simultaneously provide several functionalities. They conduct electrons and heat, maintain the mechanical integrity of the membrane electrode assembly and should maximize gas diffusivity while removing the liquid water towards the flow field channels[80, 153, 166]. Oxygen diffusivity exponentially decreases as saturation of pores with water increases[38, 41]. This is related to the blocking of available pores and a concomitant increase of tortuosity for liquid and gas transport counterflow. Focusing on the GDL, researchers have tried to optimize gas-liquid transport characteristics by finding optimal coating loads[54, 126, 167-169], understanding the effects of microstructure[170-173], developing novel coatings[61-63, 174] and using different architectures or substrates[175, 176]. A clever way for improving the gas-liquid transport consists of artificially creating pathways within the GDL for effective water removal and thereby increasing the gas diffusivity. In this direction, improvements under certain
operating conditions were measured using perforated GDLs[^64, 65, 127] and enhanced oxygen diffusivities were achieved using a locally coated GDL[^69]. Recently, we reported a method to produce GDLs with patterned wettability based on local modifications of the polymer coating’s wettability using radiation grafting[^73, 74]. Contrary to the other approaches, the radiation grafting method allows wettability modifications across the complete material thickness without altering the mechanical properties and, most importantly, it offers realistic scale-up potential. Here, we present a detailed experimental study on the ability of our newly proposed material to confine the liquid water transport to predefined pathways. This study was realized by varying different material parameters (type of carbon substrate, coating load, type of grafted compound, geometry of the water pathways). The materials were characterized by the recording of local water saturation as a function of capillary pressure in water injection experiments, where the water distribution was obtained by neutron radiography for all samples, and additionally by X-ray tomographic microscopy (XTM) for one selected sample.

### 6.3 Experimental

#### 6.3.1 Materials preparation

Toray TGP-H-060 carbon paper (~190 μm thickness and 78% porosity) was obtained from Fuel Cell Earth (Woburn, Massachusetts)[^138]. Sigracet GDL 24 AA (~190 μm thickness and 86% porosity) was purchased at Ion Power (New Castle, Delaware)[^177]. Freudenberg H2315 –H23/H24 current name– (~210 μm thickness) was obtained from QuinTech (Goepppingen, Germany)[^178].

All three types of gas diffusion layers were obtained in pristine condition (uncoated). The pristine GDLs were coated in-house with fluorinated ethylene propylene (FEP). FEP was chosen over tetrafluoroethylene (PTFE) due to its superior radiation resistance, faster grafting kinetics and superior hydrophobicity. A standard dip-coating procedure using water dispersions of FEP particles and a subsequent thermal treatment was followed, which is described in our previous work[^74, 155]. Coating loads of 5, 30 and 70% wt. were targeted (Table 6.1). Calibration curves, relating the FEP concentration in the dispersion to the final coating load, were obtained for the different GDL substrates (Appendix B, Figure 6.11).

Samples were irradiated using an electron beam in an EBLab 200 sealed laboratory emitter system from Comet AG (Flamatt, Switzerland). The details were described in our previous work[^24]. An acceleration voltage of 200 kV and a dose of 50 kGy were selected in each case. In order to create patterned materials, radiation-blocking masks
were used. The masks’ body is a 2 mm thick steel plate containing a regular arrangement of slits where the opening width coincides with the desired hydrophilic pattern width and the distance between two slits corresponds to the hydrophobic pattern width. The different pattern designs are described in Table 6.1. Masks with a slit width of 250 µm (or higher) were produced using a water jet (Waterjet AG, Aarwangen, Switzerland). For the realization of the narrowest designs (slits with a width of 100 µm), a combined water and laser cutting technology was employed (Laser MicroJet®, Synova, Ecublens, Switzerland). After irradiation, samples were rapidly stored at -80°C to reduce radical recombination prior to grafting.

Table 6.1 – Overview of samples used in this study.

<table>
<thead>
<tr>
<th>Substrate type</th>
<th>FEP coating load [%wt.]</th>
<th>Chemistry</th>
<th>Hydrophilic-hydrophobic width [µm-µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toray</td>
<td></td>
<td>FEP-g-pNVF</td>
<td>500-930</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>FEP-g-pNVF</td>
<td>500-930</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>FEP-g-pNVF</td>
<td>500-930</td>
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<tr>
<td></td>
<td>30</td>
<td>FEP-g-pAA</td>
<td>500-930</td>
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*The characterization of these samples is only presented in Supplementary Inf.

Sample used for comparison (measured with both setups, NR and XTM).
N-vinylformamide (NVF) was used as received (Sigma Aldrich 98%) without dilution. The irradiated GDLs were placed in cylindrical glass reactors, through which nitrogen was bubbled for 60 min to remove dissolved oxygen. After that, reactors were placed in a water bath at 70°C for 60 minutes. Acrylic acid (AA) was used as received (Sigma Aldrich 99%) and diluted (15% wt.) in water. A vacuum reaction system allowed for deoxygenation and application of 50 mbar abs pressure, which was needed in order to fill the hydrophobic pores and remove the trapped air. The setup and experimental procedure is described in detail in Ref. [155]. Reactions with AA were performed at 60°C for 60 minutes.

The cleaning procedure was found to be critical for the effective formation of the wettability patterns. Samples were placed in a Buchner type filter and vacuum was applied in the vessel underneath. This helps the cleaning solvent to penetrate into the inner porosity with a convective flow. 300 mL of ethanol, 300 mL of isopropanol and finally 300 mL of water were used to clean each of the grafted materials in this manner.

6.3.2 Energy-dispersive x-ray (EDX) mapping and scanning electron microscopy (SEM)

The ion exchange from H⁺ to Na⁺ was performed only for characterization purposes and does not constitute a synthetic step. The sample treated with AA was exposed to 0.05 M NaOH overnight to form the sodium acrylate salt. The Na signal produced much higher contrast in the EDX maps compared to the O signal of the non-exchanged material.

The EDX mappings were recorded using a compatible accessory (EDX TSL, AMETEK) integrated into a scanning electron microscope FE-SEM Ultra 55 (Carl Zeiss, Oberkochen, Germany). They were taken with an acceleration voltage of 10 keV, an aperture of 60 µm and gun-to-sample distance of about 9 mm. Cross sections were prepared using an epoxy resin and subsequent polishing. The method is described elsewhere [58, 61].

6.3.3 Method of standard porosimetry (MSP)

It is widely accepted that capillary pressure, $P_c$, is the driving force for liquid water transport within the GDLs [28, 179]. The method of standard porosimetry (MSP) consists of the measurement of the pore saturation, $S$, as a function of the capillary pressure and can be used with different wetting fluids [92]. Gostick et al. first adapted the method to porous gas diffusion layers for PEFCs [113]. In their experimental setup the GDL sample was sandwiched between a hydrophilic and a hydrophobic membrane [23]. The
hydrophobic membrane on top provides a very high pressure boundary which ensures the complete saturation of the GDL. In this configuration, the liquid distributor and the hydrophilic membrane beneath the sample ensures a homogeneously filled water front over the sample area. The former authors and other groups systematically obtained $P_c(S)$ relationships for different materials and studied the impact of substrate type, sample thickness, compression and sample wettability among others [93, 180-185]. Recently, Lamibrac et al. developed a setup compatible with X-ray tomographic microscopy (XTM) imaging to perform MSP measurements [26]. Compared to previous attempts [25, 186], the recent developments in terms of image processing and segmentation allowed extraction of quantitative $P_c(S)$ data from the XTM images.

In addition, in this work we adapted the previously described MSP method to inject water through a central distribution channel. In this case, the capillary pressure was controlled by regulating the liquid pressure by changing the water head. The water content was quantified using neutron radiography. A selected sample was characterized using the standard MSP setup with water over the complete bottom interface and the water distribution was imaged with XTM. All experiments were performed at room temperature.

### 6.3.4 Mono-channel injection setup

In the present work, all samples where characterized using a setup in which the injection of water was done through a channel in the center of the cell which occupies 1/10 of the sample area. This modification was introduced for two reasons: first, if water would be injected all over the area the neutron radiographs performed in the through-plane direction would contain a superimposed water layer. With the new configuration, 90% of the sample area is free of extra water. Secondly, important information relating to “lateral transport”, i.e. transport in the GDL in-plane direction, can be extracted with this setup.
Figure 6.1 - Experimental setup used in the capillary pressure experiments with neutron radiography. (a) Flow diagram of the experimental setup; (b) Cell detail showing the different elements. The GDL sample was oriented in parallel with the gravitational acceleration.

Figure 6.1.a shows the flow diagram of the setup used in all neutron radiography experiments. A water canister (30 L volume) was fixed on top of a precision motor (Berger Lahr VRDM 3913) and was connected to the main circuit (line a). The experimental sequence followed was: (I) valves V1 and V2 were switched to permit water flow through lines a-b-c to remove any gas bubbles present; (II) valves V2 and V3 were switched to permit flow through lines a-b-d-e. With the pressure sensor P1 (at a fixed distance below the injection channel) the tank height could be adjusted adequately allowing water to flow at low overpressure (less than 1 mbar); (III) after the injection channel was completely filled (verified online with neutron imaging), V3 was switched to dead-end mode where lines a-b-d were connected but without water flow; (IV) The capillary pressure, $P_c$, was calculated as $P_c = P_l - P_g$, where $P_l$ is the pressure of the liquid water immediately before the cell inlet and at the same height as the injection channel and $P_g$ is the gas pressure immediately after compartment 2. Each pressure setting was held for at least 5 minutes. The capillary pressure was varied only in increasing direction. Neutron radiographs and pressure data were acquired over the complete duration of the experiment; (V) after the data corresponding to the last capillary pressure point was acquired, compartment 1 was purged with N2 and 1 NL/min was flown through both compartments (through lines f-b-d-e and g, respectively) in order to evaporate the water from the GDL in a controlled manner (between 3-6 minutes were required to fully evaporate the water at this flowrate) so that the water footprint in the GDL during evaporation could be imaged.
The cell configuration is depicted in Figure 6.1.b. Compartment 1 contained the injection channel (1 mm width, 0.5 mm depth) in the center. A PTFE gasket of 350 μm was inserted and helped positioning the GDL. The GDL of interest (patterned GDL) was placed in compartment 1 with the direction of the pattern perpendicular to the injection channel. On top, a hydrophobic membrane (HVHP04700, Durapore) of about 120 μm thickness was placed, followed by another PTFE gasket and another GDL (plain sample and of the same substrate as the GDL in compartment 1). The reason to use a second GDL is to mimic the compression conditions existing in an actual fuel cell. The use of steel spacers and the very same GDL substrate in both compartments allowed us to adjust the GDL compression to 20% in all the experiments.

### 6.3.5 Neutron radiography (NR)

Neutron radiography was performed at the ICON beam line of the SINQ spallation source at the Paul Scherrer Institute[98]. A 20 μm thick Gd₂O₂S scintillator screen mounted in the micro-setup detector including a CCD camera (Andoe DV436, 2048 x 2048 pixels) was used for the recording of the neutron radiographs[187]. The detector pixel pitch was 13.5 μm and the effective resolution 55 μm, taking into account the unsharpness due to the beam divergence. The exposure time was set to 30 s and the readout time was 4 s. All images underwent filtering for noise removal and image correction (subtraction of the detector background and of the scattered neutrons background, correction of the beam fluctuation and of the spatial inhomogeneities), after which they were divided by an image of the dry cell to obtain the attenuation due to water only[103]. From the obtained transmission images, the quantitative water distribution was obtained by inversion of the Lambert-Beer law using a known attenuation coefficient of 4.5 cm⁻¹ for this setup (calculated from Refs.[98, 188]).

### 6.3.6 Extraction of local capillary pressure – water thickness characteristics

A study consisting of separately analyzing the water distribution above and below the injection channel showed no preferential water locations induced by height. Gravity does not seem to have a significant influence. Consequently, both domains (A<sub>above</sub> and A<sub>below</sub>) were considered when averaging attenuation (Figure 6.2.a). Hydrophilic and hydrophobic patterns were analyzed independently. Averaging areas for the hydrophilic and hydrophobic lines were chosen as bands having half of the width of the corresponding region (see Figure 6.2.b). Following this procedure, we extracted averaged attenuations (representative of the whole sample) for these areas and converted them to a water thickness as described in the previous paragraph. In all NR
experiments water thickness values are provided instead of saturation, because calculating the latter requires precise knowledge of the porosity and thickness of the compressed sample, which are difficult to estimate as a function of coating load, grafting treatment, and effective compression.

Figure 6.2 - (a) Neutron radiograph showing the regions used for extracting the attenuation data. The GDL orientation (with respect to gravitational acceleration) is the same as shown in the radiograph; (b) Detail showing the averaging intervals for one hydrophilic domain and two hydrophobic domains.

6.3.7 Homogeneous injection setup

The experimental setup and procedure has been extensively described previously and was used identically in this work[26]. The GDL sample is sandwiched between two membranes: a hydrophilic membrane (pore size 0.22 μm) generates homogeneous injection of water from the bottom side, while a hydrophobic membrane on top confines the water and allows for saturations beyond the bubble point. Two consecutive cycles of imbibition (increasing $P_c$) and withdrawal (decreasing $P_c$) were performed, but only imbibition results are presented for the sake of clarity. X-ray tomographic
microscopy (XTM) imaging was made at the TOMCAT beamline of the Swiss Light Source (SLS) with a beam energy of 13.5 keV. Tomographic scans with 2001 exposures of 10 ms were performed resulting in a scanning time of 20 s. The PCO edge camera and 2-4x zoom microscope system was used so images were obtained with a pixel/voxel size of 2.2 μm. More details on image processing, segmentation and derivation of the saturation vs. capillary pressure curves were extensively described by Lamibrac et al.[26]. One sample (Toray 70%FEP-<sub>pNVF 500</sub>-<sub>930μm</sub>, see Table 1) was analyzed with this setup.

6.4 Results and Discussion

6.4.1 Resolution assessment of the grafted pattern

Before presenting the results of the capillary pressure measurements on the modified materials, we show an ex-situ analysis of the obtained hydrophilic patterns. Figure 6.3.a shows a regular optical image of a modified sample after immersing it in water. Water accumulates at the hydrophilic patterns on both the top and bottom surface. A closer look with an optical microscope confirms the localization of water (Figure 6.3.b). EDX mapping allows for identification of the grafterd molecules’ distribution. The carbon signal is mainly derived from carbon fibers and, to a lesser extent, the coating, while the fluorine signal originates from the FEP polymer (Figure 6.3.c). The sodium signal comes exclusively from sodium polyacrylate salt formed during ion exchange in aqueous NaOH. The sodium mapping shows that grafted polyacrylic acid is located in a narrow space of about 100 μm width on the available coating surfaces (Toray 70%FEP-<sub>pAA 100</sub>-<sub>500μm</sub>). Figure 6.3.d shows the averaged Na-intensity from the EDX mapping from top and bottom surfaces of a modified sample. The top surface refers to the GDL surface directly exposed to the electron radiation. Despite the intrinsically irregular nature of the material, there is a fairly good agreement between both signals. The fact that the bottom surface (opposite to the irradiated surface) presents a similarly modified pattern suggests that the electron beam activation effectively occurs without significant detrimental scattering effects. In order to validate that grafting polymerization happens throughout the bulk of the material, electron microscopy of cross-sections (prepared via embedding in an epoxy resin) was performed (Figure 6.3.e and 6.3.f). The use of the secondary electron detectors showed notable contrast variations between original coating (FEP) and grafted copolymer (FEP-g-pAA). This distinction is probably due to the difference in electrical conductivity, as reported in previous works[139, 155].
Figure 6.3 - (a) Water accumulation in the hydrophilic patterns. Sample: Freudenberg 30%FEP-g-pNVF 500-930μm); (b) Closer look at the water accumulation on the hydrophilic pattern using an optical microscope; (c) EDX mapping showing the fibers (carbon signal), the coating (fluorine signal) and the grafted regions (sodium signal). Sample: Toray 70%FEP-g-pAA 100-500μm with sodium replacement; (d) Averaged sodium intensity profile of the EDX elemental mapping of the top and bottom surfaces; (e) SEM image (secondary electrons detector) of a cross section showing two hydrophilic patterns. Sample: Toray 30%FEP-g-pAA 500-930μm; (f) Details of a cross section demonstrating that the coating modification occurs through the complete material thickness.

6.4.2 Variation of material parameters

Figure 6.4 presents a collection of water thickness vs capillary pressure curves for the most relevant materials. The graphs have been organized in the following fashion: in vertical alignment (Figures 6.4.a, 6.4.d and 6.4.f) three different substrates (SGL, Toray and Freudenberg) are compared. In horizontal alignment (Figures 6.4.c, 6.4.d and 6.4.e) a study with three coating loads (5, 30 and 70%wt. FEP) is provided.
Figure 6.4 - Water thickness versus capillary pressure curves of differently modified materials. The blue filled symbols represent hydrophilic domains while empty black symbols the hydrophobic domains. Red squares represent points of measurements on corresponding untreated samples (baselines).
Diagonally, a comparison (Figures 6.4.d and 6.4.b) of the chemistry used (NVF or AA) for grafting polymerization is presented. Last, we study (Figures 6.4.e, 6.4.g, 6.4.i and 6.4.h) the influence of the hydrophilic pattern width where three patterns (500-930, 250-460 and 100-500 µm) are compared. The effect of varying the substrate (Toray and Freudenberg) is studied using the narrowest pattern as well (Figures 6.4.i and 6.4.a). Figure 6.5 is organized in the same way and contains neutron radiographs at selected $P_c$ (indicated in Figure 6.4). The impact of the parameter variations is presented and discussed in the following paragraphs.

**Figure 6.5** - Neutron radiographs at selected capillary pressures (shown in Figure 6.4) for differently treated materials.
6.4.3 Influence of substrate

Figure 6.4.d shows the $P_c$ characteristic of a Toray 30%FEP-g-pNVF 500-930μm. In this case, the hydrophilic domains are nearly saturated at 20-25 mbar, while water content in the hydrophobic domains remains low (Figure 4d). The $P_c$ characteristic of the baseline material (Toray 30%FEP untreated) showed that much higher $P_c$ is required to fill the GDL sample (i.e. it is still nearly empty at 40 mbar), which shows the influence of the hydrophilic patterns into the hydrophobic domains. The neutron radiograph shows well-defined water filled patterns of 500 μm width (the dashed lines indicate the original line width) at 25 mbar (Figure 6.5.d). The Freudenberg 30%FEP-g-pNVF 500-930μm characteristic is plotted in Figure 6.4.f. With this substrate, higher $P_c$ is needed to fill the hydrophilic patterns (>40 mbar) while the hydrophobic domain remains almost dry. Perfectly defined water channels are observed (Figure 6.5.f). The corresponding baseline material (Freudenberg 30%FEP untreated) also shows that higher pressure is needed to imbibe the sample with water (as compared to the hydrophobic domains of the treated sample).

The capillary pressure characteristic of SGL 30%FEP-g-pNVF 500-930μm reveals no sign of patterned water distribution (Figure 6.5.a); therefore only an average water thickness (for the whole sample area) is herein provided (Figure 6.4.a).

The impossibility of forming patterns using the SGL substrate material (Figure 6.4.a and 6.5.a) in the capillary pressure experiment highlights the relevance of the microstructure for the water transport. Even when a high coating load was used (SGL 70%FEP-g-pNVF 250-460μm), a very similar behavior is observed when imbibing the SGL material (Appendix B, Figure 6.12). We were able to give proof of the presence of hydrophilic patterns in the modified SGL material both by chemical mapping with EDX and by immersing the material in water and clearly observing water accumulation on the hydrophilic patterns (Appendix B, Section 6.13). However, the observation of the water distribution during imbibition suggests that water preferentially fills the larger pores, which are randomly distributed throughout the material. The location of the pores filled first does not necessarily coincide with the existing hydrophilic pattern. This observation points to the fact that large pores – even if hydrophobic – are filled at lower (or similar) pressures than small hydrophilic pores.

This is contradictory to the expectations if considering the Washburn equation (see Appendix A, Section 6.6), which predicts a negative capillary pressure for any hydrophilic pores and a positive capillary pressure for any hydrophobic pores. The Washburn equation is, however, derived from capillary geometries that do not feature the constrictions between pores which are typical of fibrous materials. In this paper the
Young-Laplace equation is derived for a cylindrical pore with a variable constriction diameter (Figure 6.6.a). With this approximation we do not claim to provide a fully accurate representation of an actual GDL which is much more complex, but to include a straightforward theoretical basis to explain experimental observations that might seem counterintuitive.

![Illustration of the geometry considered for the capillary pressure model](image)

**Figure 6.6** - (a) Illustration of the geometry considered for the capillary pressure model; (b) Calculated values of capillary pressure versus $d_{\text{min}}/d_{\text{max}}$ for different contact angles and $d_{\text{max}}$.  

\[ P_c \text{ [mbar]} = \text{function of } d_{\text{min}}/d_{\text{max}} \text{ and } \theta \]
$P_c$ vs $d_{\text{min}}/d_{\text{max}}$ curves for various contact angles and pore diameters are represented in Figure 6.6.b. It can be seen that at a given value of $d_{\text{min}}/d_{\text{max}}$, the $P_c$ dependence on contact angle is much greater for smaller pore radii. For the case of $d_{\text{max}}=200\mu\text{m}$, the influence of contact angle is much less significant. This could explain the reason behind the rather arbitrary water filling of SGL materials. Lamibrac et al. recently extracted pore size distribution for SGL and Toray materials using XTM data\cite{26}. They demonstrated that SGL 24BA presents a much broader pore size distribution compared to Toray TGP-H-060. Additionally, SGL contains a notable number of rather wide pores (range of 200 $\mu\text{m}$ diameter) which do not exist in the Toray or Freudenberg materials. Parikh et al. extracted pore size distribution of SGL, Toray and Freudenberg materials from scanning electron microscopy\cite{189}. An average pore diameter of 31.8, 26.4 and 16.5 $\mu\text{m}$ was obtained for SGL, Toray and Freudenberg, respectively. Freudenberg seems to present the narrowest pore size distribution, followed by Toray and finally SGL. This means that the Freudenberg substrate contains the smallest pores and that the pore size is most uniform within this series. The minimal contact angle obtained by grafting pNVF onto FEP is $20^\circ$, but we assume a higher contact angle of $\theta = 60^\circ$ for the hydrophilic pores due to the limited coverage of carbon fibers\cite{188}. Similarly, we assume an internal contact angle of $\theta = 110^\circ$ for the hydrophobic pores. The results shown in Figure 6.6.b highlight that large pores, even if hydrophobic, can be filled at a lower (or similar) pressure than hydrophilic but smaller pores (at a wide range of $d_{\text{min}}/d_{\text{max}}$). It should be furthermore considered that the flake-like binder, which covers a significant fraction of the carbon fibers in an SGL substrate, presents additional complications to the water transport modelling, since we have no information about the wettability of the binder surfaces with respect to the carbon fiber and/or coating, nor how the coating specifically covers each of these features.

The tendency herein observed also explains why a higher capillary pressure is required to fill the hydrophilic domains in the modified Freudenberg materials compared to those of the modified Toray GDLs (Figure 6.4.f and 6.4.d). Again, this is contradictory to the predictions of the Washburn equation, which would predict a negative pressure for all hydrophilic pores.

It is worth mentioning that the calculations performed herein (Figure 6.6) provide an approximate estimation of the penetration capillary pressure for different geometries and surface properties. Therefore, a more detailed modelling approach, such as the pore network modeling or full morphology (Lattice Boltzmann) simulations\cite{37, 190-193} would bring a more realistic description of the phenomena.
6.4.4 Influence of coating load

Focusing on Toray as GDL substrate, the effect of the polymeric coating load was studied (Figures 6.4.e, 6.4.d and 6.4.e). When using low FEP amounts (5%wt.), there is nearly no difference between the capillary pressure characteristics in hydrophobic and hydrophilic domains (Figure 4c). As previously described, the modified sample with 30%wt. of FEP (Figures 6.4.d and 6.5.d) shows clearly defined patterns with the hydrophilic domains being nearly filled at 25 mbar. Interestingly, the increase of coating load to 70%wt. slightly reduces the capillary pressure necessary to fill the hydrophilic domains (~16 mbar), while the water content in the hydrophobic regions is virtually zero for pressures below 40 mbar (Figure 6.4.e). Thus, the water segregation into hydrophilic and hydrophobic domains is significantly more pronounced in the material with the higher coating load (Figure 6.5.e). The probable reason for the impact of coating load is the change of coverage of the carbon fibers (Figure 6.7), resulting in a decreasing internal contact angle for increasing loads in the hydrophilic regions.

![Diagram showing the effect of coating load on carbon fiber coverage by coating and subsequent grafting.](image)

**Figure 6.7** - Illustration showing the effect of coating load on carbon fiber coverage by coating and subsequent grafting.

The coexistence of surfaces with different wettability gives rise to the so-called mixed wettability\(^{194}\). The contact angle of Toray (uncoated) fibers was found to be around
80°[52], while the contact angle of the pNVF grafted FEP is around 20°[159]. The assumption of a decreasing contact angle (in the grafted regions) with increasing coating load is in line with the observations made in our previous work. It was proven that higher coating loads (with the very same chemical modification) led to faster wetting dynamics[155]. This was explained by the increase of carbon fiber surface coverage and a concomitant increase in overall (or average) hydrophilicity. A similar effect can be expected in the opposite direction for the hydrophobic regions: the contact angle should increase with the coating load, as a result of the mixed wettability between the carbon fibers (~80°) and the untreated FEP (~110°). Based on the $P_C$ calculations for different internal contact angles (Figure 6b), the improved segregation for higher coating loads can be explained by these changes in contact angle, as the capillary pressure is generally positive except for very hydrophilic materials (e.g. 40°) and highly dependent on the effective internal contact angle.

### 6.4.5 Influence of hydrophilic pattern width

The capillary pressure characteristic of materials with different pattern width (Figure 6.4.e, 6.4.g, 6.4.i) show an interesting trend: the narrower the hydrophilic pattern, the higher the $P_C$ required for imbibition of the hydrophilic regions. As a logical consequence, the separation between hydrophobic and hydrophilic domains is less defined for thin patterns (Figures 6.5.e, 6.5.g and 6.5.i). For the thinnest lines (100 μm), although a faint pattern is still visible, the analysis of neutron radiographs shows that the width of the water filled region is approximately 250 μm, which is clearly larger than the grafted region. Assuming that wettability of the hydrophilic domains is the same in every case, the explanation has to be associated with microstructural details. In order to provide a water pathway, a continuous network of connected pores with reasonably large throat sizes needs to be available. The probability of providing such a network is evidently higher for wide hydrophilic domains. For thin domains, the probability increases that the pathway is obstructed by a barrier of small throats creating a bottleneck which requires a higher capillary pressure to overcome. We further analyzed the case of 100 μm thin hydrophilic domains with another substrate (Freudenberg 70%FEP-g-pNVF 100-500μm), with the results presented in Figures 6.4.h and 6.5.h. In this case, the water segregation between hydrophobic and hydrophilic domains is slightly better, which can be attributed to two reasons (Figure 6.8). First, the capillary pressure in the hydrophobic regions is higher due to the smaller average pore size. Second, the smaller pore size and narrower pore size distribution of this substrate reduces the probability of having a bottleneck along the water pathway.
Figure 6.8 - Neutron radiographs of imbibition (at three capillary pressures) and drying experiments of two different samples: Toray 70%FEP-g-pNVF 100-500μm (top), Freudenberg 70%FEP-g-pNVF 100-500μm (bottom).

6.4.6 Water distribution during evaporation

The observation of water distribution during the removal by evaporation gives interesting further insight. In an operating cell, the phenomenon of water evaporation and condensation also plays a crucial role in the cell water balance. We observed that, when flowing dry gas through both compartments, the water occupying the hydrophobic regions is rapidly removed (in less than 2 minutes) in the case of the two modified materials (modified Toray and Freudenberg substrates with 100 μm hydrophilic patterns), while the hydrophilic patterns remain with a substantial water content for a longer time (4-6 minutes), being gradually dried. As shown in Figure 6.8, the water separation between hydrophilic and hydrophobic domains is much clearer during evaporation than during imbibition. These results confirm that we have well-defined hydrophilic and hydrophobic regions and support the previous explanations for the poor formation of pathways in imbibition experiments: contrary to these, evaporation does not rely on the overcoming of barrier capillary pressures. While the contact angle might only indirectly influence the evaporation rate, it is clear that the hydrophobic regions dry faster than the hydrophilic ones. For a given water volume, a water droplet in a hydrophobic domain exposes a higher surface area to the gas flow due to its curvature, therefore facilitating the evaporation process. This and the probably preferential location of water in the larger pores favor the evaporation in the hydrophobic domains first. When the water saturation is reduced, gas flow (convection) is facilitated and therefore evaporation is further favored.
6.4.7 Influence of grafted compound

Another study involves the variation of the chemical treatment used for grafting. Figure 4b shows the capillary curves when acrylic acid is used as a hydrophilic monomer instead of N-vinylformamide. Compared to the latter (Figure 6.4.d), a higher pressure is needed to fill the hydrophilic pathways (~40 mbar) with the filling of the hydrophobic regions following just after. Therefore, poorly defined patterns were observed in the neutron radiographs (Figure 6.5.b). It must be mentioned that, from the water thickness measured, we suspect that this particular sample was too compressed (~20% lower thickness), which might increase the differences due to the reduction of the pore size. Nevertheless, as the compression affects both the hydrophilic and hydrophobic regions, it cannot explain completely the differences to the base case. The effects derived from the two different chemical treatments are rather straightforward. The reason is the different intrinsic contact angles provided by the two chemistries. Measurements on flat surfaces revealed that the contact angle could be decreased from initial values of ~110° (FEP surface) to ~20° in the case of FEP-g-pNVF and ~50° for FEP-g-pAA. At a given constriction diameter (i.e. $d_{\text{min}}/d_{\text{max}}=0.7$), a difference in $P_c$ of approximately 25 mbar more is required to fill a pore grafted with acrylic acid compared to a pore treated with N-vinylformamide. These results highlight the relevance of, not only the wetting strength of the hydrophilic regions, but the ratio between both hydrophilic and hydrophobic regions’ wettability in the water distribution.

6.4.8 Influence of the injection mode

For one selected sample (Toray 70%FEP-g-pNVF 500-930μm) we performed a comparative analysis using homogeneous water injection and high resolution XTM. As explained in the experimental section, water was injected over one face of the material in this case. The separate analysis of hydrophilic and hydrophobic regions (Figure 6.9.a) shows that already at negative capillary pressures (~ -14 mbar) the hydrophilic patterns are nearly filled. The maximum saturation is reached at about 10 mbar, while the water content in the hydrophobic regions still remains close to zero. At 20 mbar, the hydrophobic regions start imbibing and filling is completed at pressures higher than 60 mbar.
Figure 6.9 - Capillary pressure characterization of Toray 70%FEP-g-pNVF 500-930μm with homogeneous injection characterized with XTM. (a) Saturation versus capillary pressure curves. (b) XTM radiographs of three different slices (bottom, middle and top of the GDL sample) at four $P_c$ (-14, 5, 30 and 50 mbar). The irradiated side of the GDL was placed towards the injection interface (bottom).
The three dimensional nature of the tomographic imaging allows a detailed analysis over the thickness of the material. Slices at three different positions (one near the injection surface, one in the middle of the sample and one near the top) at four different capillary pressures are presented in Figure 6.9.b. The radiographs taken at -14 mbar showed that almost completely filled hydrophilic lines (of about 550 µm width) appear near the injection membrane, while the hydrophobic areas are completely water-free. A slice through the center of the GDL shows partially filled hydrophilic patterns of about 400 µm width, while the slice near the top (near the hydrophobic membrane) shows only some pores filled with water in the hydrophilic regions, which proves that breakthrough readily happens at negative capillary pressure. At 5 mbar, a width of the water-filled region of about 700 µm is measured at the bottom interface, and of 580 µm and 500 µm in the center and top slice, respectively. At increased $P_c$ (30 mbar), the bottom interface appears nearly filled with water while significant pattern spreading occurs having wider water filled domains of about 800 and 700 µm width at the center and top slice, respectively. At higher $P_c$, a further broadening of the water filled regions is observed.

The differences of $P_c$ necessary to fill the hydrophilic lines between XTM and NR experiments (-14 mbar for the homogeneous injection and +16 mbar for the central injection) can be explained by the anisotropy of the material\footnote{26}, resulting in important differences in the in-plane and through-plane water transport characteristics. In order to verify that they do not originate from other differences in the experimental setup, an analysis of the water distribution in the region which is in contact with the injection channel was performed (for the measurements using the NR setup).

$P_c$ [mbar]

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**Figure 6.10** - Neutron radiographs on the injection channel area of Toray 70%FEP-g-pNVF 500-930µm at five different capillary pressures (1, 5, 30, 50 and 95 mbar).
The difficulty of analyzing quantitatively the water content over the injection channel is a result of the 0.5 mm water column superimposed to the porous GDL, which significantly increases the error of the measurement. However, qualitative water distribution could be extracted (Figure 6.10). The differences between hydrophobic and hydrophilic regions show that the hydrophilic lines do get filled at pressures as low as 1 mbar (due to the absence of a hydrophilic membrane, negative pressures were not possible with this setup). Furthermore, the pattern widths measured at various capillary pressures matches very well the measurements performed with XTM (Figure 6.9). Although the hydrophilic patterns under the rib appear to be filled at very low $P_c$, a higher pressure is required to fill the adjacent areas. This result confirms that the observed differences are mainly due to the direction of injection and not to other parameters related to experimental configuration.

### 6.4.9 Implications for fuel cell operation

The prediction of fuel cell performance from capillary pressure data (measured in such an *ex situ* experiment) is rather challenging. However, the results obtained shed light on two types of water transport characteristics. The mono-channel water injection forces water to travel longer distances and it is limited by the transport in lateral direction (*in-plane*), where pores are generally smaller, while the homogeneous injection setup focuses on *through-plane* transport characteristics. Both transport direction are relevant for the removal of water during fuel cell operation because, although the water is produced over the complete area, it can only be removed via the flow channels. The capillary pressure needed to fill the hydrophilic pathways is not expected to be limiting, as the electrochemical production of water can easily match the slight increase of pressure. A much more important characteristic is, at the point where the hydrophilic pathway is established, the level of water saturation in the hydrophobic regions dedicated to gas transport. Thus, the materials providing a good separation between hydrophobic and hydrophilic regions are expected to be the most suitable, even if they require higher absolute capillary pressure. According to this study, this requirement is obtained with materials having smaller pores and high coating loads. A further aspect is obviously the diffusivity of oxygen on the hydrophobic regions: even if they are not filled with water at all, the use of high coating loads might detrimentally affect this parameter. Thus, further improvements of the coating techniques to provide homogeneous coverage of the carbon fibers with a minimal amount of coating are highly desired. Nevertheless, the question of the actual fuel cell performance cannot be answered based on the *ex situ* characterization only. In the follow-up work (Part III of this series), *in situ*
electrochemical characterization of operating cells combined with neutron radiography is provided and these questions are addressed.

Besides the application of our materials to reduce mass transport losses, a further possibility is to use it as a water distributor in evaporatively cooled fuel cells. In such systems, water is injected into the cell as a liquid and evaporates to remove heat\[^{195, 196}\]. Using our material, an effective distribution of the liquid from injection channels over the cell area is expected\[^{23}\]. In this case, the lateral transport is the parameter having the highest importance.

### 6.5 Conclusions

We have demonstrated the ability of GDLs with patterned wettability – having hydrophilic pathways dedicated to the removal of water – to confine water within the predefined pathways, although this ability heavily depends on a variety of material parameters. The main findings concerning the impact of these parameters are:

- Regular structures with low average pore size favor the patterning. While the materials based on Toray and Freudenberg substrates yield clearly defined domains, the materials based on SGL substrates – having a broad pore size distribution – show a much more random distribution of water without preferential water locations.
- Low coating loads do not permit a clear formation of water pathways.
- Narrow patterns lead to loosely defined water pathways, although the high resolution of the material modification was confirmed by SEM-EDX analysis. They also result in an increase of the capillary pressure required to fill the hydrophilic regions.
- The chemical treatment to produce hydrophilic surfaces has a major impact. Materials grafted with N-vinylformamide (providing contact angles of approximately 20°) have much better defined domains than materials treated with acrylic acid (contact angle of 60°).
- When water is injected homogeneously over one side of the GDL, the capillary pressure curves shift to lower pressure values compared to the central monochannel configuration. This emphasizes the important differences in the characteristics of through-plane and in-plane water transport.
6.6 Appendix A – Calculation of capillary pressure

The Young-Laplace equation relates the capillary pressure with the surface tension and mean curvature of the separating interface\[29\]. For cylindrical capillary tubes, the capillary pressure can be calculated as:

\[ P_c = \frac{-2\gamma \cos \theta}{r} \]  \hspace{1cm} (6.1)

where \( \gamma \) is the surface tension, \( \theta \) the contact angle of water with the solid wall and \( r \) the pore radius. Dullien et al. considered a conical capillary\[197\]. We propose an extension of the cylindrical model to account for a variable constriction diameter (Figure 6.6.a). This involves calculating a new angle, \( \alpha \), determined by the pore wall and the cylinder axis. If \( r(x) \) is the variable pore radius, \( \alpha \) can be calculated as:

\[ \alpha = \tan^{-1}\left(\frac{dr}{dx}\right) \]  \hspace{1cm} (6.2)

The relevant water contact angle, \( (\alpha + \theta) \) can be introduced in the Washburn equation leading to:

\[ P_c = \frac{-2\gamma \cos\left(\tan^{-1}\left(\frac{dr}{dx}\right) + \theta\right)}{r} \]  \hspace{1cm} (6.3)

For a given constriction (or obstruction), we found the minimum value of \( P_c(x) \). For the results presented in this paper we used a sinusoidal profile with \( d_{\text{max}} = 30 \ \mu m \) and \( L = 20 \ \mu m \) (Figure 6.6.b). The value of \( L \) was chosen to have a constriction width in the range of a typical GDL carbon fiber.
6.7 Appendix B – Supplementary material

6.7.1 Section S1: Coating load calibration curves

Figure 6.11 - Calibration curves relating the FEP coating load in the final GDL with the percentage of FEP121 (dispersion) in water for the three different GDL substrates: Freudenberg, Toray and SGL.
6.7.2 Section S2: Imbibition of SGL 70%FEP-g-pNVF 250-460 µm

Figure 6.12 - Water thickness versus capillary pressure of SGL 70%FEP-g-pNVF 250-460 µm. Neutron radiographs at two capillary pressures (4 and 40 mbar) and two different drying times are included. The imbibition results show lack of water patterning and the water distribution under drying conditions indicates some preferential water locations (corresponding to hydrophilic regions), however rather poorly.
6.7.3 Section S3: Hydrophilic patterns on SGL 30%FEP-g-pNVF 500-930 μm

**Figure 6.13** - Modified SGL 30%FEP-g-pAA 500-930 μm. (a) Picture showing the water accumulating on the hydrophilic patterns. (b) EDX elemental mapping of carbon, fluorine and sodium.
Chapter 7. **In situ** characterization

The previous chapter discussed the water transport in modified gas diffusion layers using an *ex situ* method for obtaining the capillary pressure characteristic. From that study successful candidates providing the best water segregation were selected to perform *operando* testing. This chapter focuses on *in situ* characterization of polymer electrolyte fuel cell devices containing gas diffusion layers with patterned wettability.

Using the multicell setup, which allows simultaneous operation of six cells, we have systematically compared the influence that various cathodic gas diffusion layers have on fuel cell performance. The pulsed gas analysis method, which allows assessing different mass transport indicators, was used in combination with neutron radiography to image the water distribution under operation. The effect of various patterns and the influence of adding a microporous layers were evaluated using different operating conditions.

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7.1 Abstract

Following our two previous publications on material synthesis and on ex situ characterization, we present an experimental in situ study to evaluate the effects of using gas diffusion layers with patterned wettability at the cathode side of polymer electrolyte fuel cells. The operando performance was assessed using traditional electrochemical diagnostics (such as polarization curves) combined with the pulsed gas analysis (PGA) method, which allows measuring the mass transport losses. Neutron radiography was performed simultaneously in order to image the water distribution during operation. Using this methodology, the effects of changing the pattern, including a microporous layer (MPL), and varying the operation conditions (temperature and relative humidity of the cathode gas) have been systematically evaluated. It has been confirmed that water redistributes according to the engineered pattern and that the power density is significantly increased thanks to reduced mass transport losses under various conditions.

7.2 Introduction

Several attempts have been reported in the literature to develop porous materials for fuel cells with optimized liquid/gas transport characteristic\[153, 166\]. The variation of microstructure\[171, 172\] and the optimization of hydrophobic coatings and their content permitted significant improvements in performance\[58, 61-63, 167\], while the inclusion of microporous layers led to the state-of-the-art materials that we know today\[16, 18, 55, 198-202\]. However, these materials do not have dedicated pathways for liquid and gas transport, but randomly distributed transport paths defined by the pore size and coating distributions.

The perforation of GDLs in specific locations showed improved performances under certain operating conditions\[64, 65\]. The local application of hydrophobic coatings was reported to improve oxygen diffusivity using an ex situ test rig combined with X-ray tomography\[67-69\]. An in situ study by the same research group demonstrated clear improvements when combining these hybrid GDLs with micro-grooved gas channels, but the isolated effect of hybrids GDLs did not lead to significant performance improvements\[70\]. Recently, we reported a method to produce GDLs with patterned wettability\[73, 74\] based on radiation induced chemical grafting, and were the first to publish operando data with such patterned materials, showing a significant improvement when using them on the cathode of a PEFC\[74\].

Here, we present a comprehensive study on the impact of GDLs having patterned wettability on the water distribution and performance of the cell. The varied parameters include the dimensions of the pattern, the presence or absence of an MPL, and
operating parameters such as humidity and temperature, respectively. This work currently rounds up a series of three papers including a detailed study on the material synthesis parameters (Part I)\textsuperscript{[155]} and the analysis of the impact of various material parameters (substrate, coating load, grafting chemistry, pattern dimensions) on the water distribution in capillary injection experiments (Part II)\textsuperscript{[157]}.

7.3 Experimental

7.3.1 Materials

Toray TGP-H-060 was used as a substrate for all the experiments. All samples were coated with 30\%wt. fluoroethylene propylene (FEP) using the dip coating method. Details about the coating application can be found in our previous work\textsuperscript{[74, 155]}. The coated GDLs were then irradiated using masks (stainless steel, 2 mm thick) with two different designs: 1) 500 \(\mu\)m openings spaced 930 \(\mu\)m and 2) 250 \(\mu\)m openings spaced 1000 \(\mu\)m. The first design provided a hydrophilic areal fraction of 35\% and the second a fraction of 25\%. A laboratory device (EBLab, Comet AG, Switzerland) was used for sample electron irradiation following the same procedure described previously\textsuperscript{[74, 157]}.

N-vinylformamide (NVF) was used as hydrophilic monomer for the grafting reaction. It was used as received without further dilution (Sigma Aldrich, 98\% purity). The previously irradiated materials were exposed to the monomer in absence of oxygen at 70°C and atmospheric pressure during 60 minutes. The materials were cleaned after grafting following the procedure described in our previous work\textsuperscript{[24]}.

The baseline material used for comparison was unmodified Toray TGP-H-060 carbon paper with 30\%wt. FEP coating. The baselines and modified material provide from the very same batch of coated substrate GDLs. This allowed us to isolate the effect of producing hydrophilic patterns without any other significant influencing parameter such as substrate microstructure, coating load or distribution, etc. Self-standing microporous layers (MPL) (Carbel CB30Z, Gore) were used.

7.3.2 Cell configuration and setup

Our previously introduced multicell setup\textsuperscript{[15]} was used for all the experiments reported here. A simultaneous operation of six cells is possible with this setup while being compatible with neutron imaging in both imaging configurations (through-plane and in-plane). Pure hydrogen and air were supplied to anode and cathode, respectively. A single gas mixing and humidifier system is used for all 6 cells, ensuring that all cells are fed
with gases having the very same concentration and humidity. However, the flow rates for the anode and cathode can be adjusted individually for each cell and were set to 0.4 NL min\(^{-1}\) (anode) and 1.0 NL min\(^{-1}\) (cathode). This translates to very high stoichiometries (\(\lambda > 60\) at 1 A cm\(^{-2}\)) to allow for the so-called “differential cell” operation\(^{[54, 203]}\).

The individual cells were machined in aluminum and coated with a protective layer (25 \(\mu\)m Ni, 10 \(\mu\)m Au). They have 1 cm\(^2\) of active area and the flow field is composed of five parallel channels (1 mm wide, 0.55 mm deep) separated by 1 mm lands. Catalyst coated membranes (CCM) (Primera 5710, W.L. Gore & Associates, Inc. USA) with catalyst layers (CL) containing Pt loadings of 0.1 mgPt cm\(^{-2}\) on the anode and 0.4 mgPt cm\(^{-2}\) on the cathode, respectively, were used for every experiment. While on the anode only the baseline GDL material was used, on the cathode the baseline and the two different modified materials were employed. The cells were either assembled without MPL, or with an MPL on both sides. The materials combinations for all 6 tested cells are summarized in Table 7.1. The GDL compression was set to 20% for every experiment. PTFE gaskets of 350 \(\mu\)m thickness and steel spacers (of variable thickness) were used for positioning, tightening and for adjusting the compression.

**Table 7.1 – Collection of GDL and MPL materials used.**

<table>
<thead>
<tr>
<th>GDL(_{an})</th>
<th>GDL(_{ca})</th>
<th>MPL(<em>{an})/MPL(</em>{ca})</th>
<th>Nomenclature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toray 30%FEP</td>
<td>Toray 30%FEP</td>
<td>No/No</td>
<td>Baseline</td>
</tr>
<tr>
<td>Toray 30%FEP</td>
<td>Toray 30%FEP-g-pNVF</td>
<td>No/No</td>
<td>Patterned 500</td>
</tr>
<tr>
<td></td>
<td>500-930(\mu)m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toray 30%FEP</td>
<td>Toray 30%FEP-g-pNVF</td>
<td>No/No</td>
<td>Patterned 250</td>
</tr>
<tr>
<td></td>
<td>250-1000(\mu)m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toray 30%FEP</td>
<td>Toray 30%FEP</td>
<td>Yes/Yes</td>
<td>Baseline+MPL</td>
</tr>
<tr>
<td>Toray 30%FEP</td>
<td>Toray 30%FEP-g-pNVF</td>
<td>Yes/Yes</td>
<td>Patterned 500+MPL</td>
</tr>
<tr>
<td></td>
<td>500-930(\mu)m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toray 30%FEP</td>
<td>Toray 30%FEP-g-pNVF</td>
<td>Yes/Yes</td>
<td>Patterned 250+MPL</td>
</tr>
<tr>
<td></td>
<td>250-1000(\mu)m</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
7.3.3 Experimental protocol

Two types of experimental protocols were used: 1) the recording of polarization curves (referred to as IV curves) and 2) the variation of cathode relative humidity (RH) at a fixed current density (referred to as RH series in this work). The IV curve experiments consisted of, at least, 10 to 12 current points in increasing fashion. The RH series experiment consisted of setting a certain current density (0.5, 0.75 and 1.25 A cm\(^{-2}\) depending on the experiment), an anodic RH (RH\(_{an}\)) of 100\%, and recording the voltage response at five different (0, 40, 60, 80 and 100\%) cathodic RH (RH\(_{ca}\)). The holding time per data point for all the experiments was 20 minutes.

The pulse gas analysis method (PGA) was applied to each data point recorded. The PGA method consists of the switching of the air flow in the cathode to a flow of helox (21\% \(\text{O}_2\), 79\% \(\text{He}\)) or pure oxygen. Due to the superior oxygen diffusivity in helium compared to nitrogen (a factor 2 to 3), an indicator called “bulk-losses” is calculated from the difference of cell voltage under air and helox. The bulk mass transport losses are normally related to diffusive transport limitations in large pores (GDL). The “non-bulk” losses are obtained from the difference of cell voltages under pure oxygen and helox and are related to diffusive transport limitations in the Knudsen regime (pores in the 10 nm range) or through thin films of ionomer/water in the catalyst layer. Under pure oxygen the mass transport losses are nearly zero but a correction for higher partial pressures needs to be accounted for (45 mV increase due to changes in the Nernst potential and the reaction kinetics). The test-bench used in this study permitted supplying the alternate gases (helox/oxygen) for short intervals of 1 second, hence the name pulse gas analysis. The use of this pulsed method was shown to be essential to avoid measurement artefacts (dry out and changes in catalyst coverage) associated with continuous operation with helox or \(\text{O}_2\). A detailed explanation of the method can be found in our previous paper[101].

7.3.4 Imaging setups

The neutron radiography experiments were performed at the ICON beamline\[98\] of the Swiss Spallation Neutron Source (SINQ) at the Paul Scherrer Institut. Two different imaging configurations (Figure 7.1) were used: through-plane imaging (membrane perpendicular to the beam axis) and in-plane imaging (membrane parallel to the beam axis).
Figure 7.1 - (a) Illustration showing the two imaging modes used in this work: beam perpendicular to the membrane plane (through-plane) and parallel to the membrane (in-plane). An example of the type of images obtained using both imaging configurations is shown. (b) Cutoff of 5 channels to show the differences between calculating the pixel-wise median projection and average projections.

In the through-plane experiments, a conventional neutron imaging setup was used with a neutron sensitive scintillator screen ($^6$LiF/ZnS, thickness 50 $\mu$m) perpendicular to the beam axis. A cooled CCD camera (Andor iKon-L, 2048x2048 pixels) was used together
with optical lenses (Zeiss Makro-Planar, 100 mm focal length). The resulting pixel size was 62.5 µm, translating to a maximal field of view of 12.8 x 12.8 cm², and the effective resolution including blurring was 115 µm (defined by the half period of the 10% MTF cutoff). With a beam collimation of 400 (defined by the ratio of the source-sample distance L and the source size D) and a sample-detector distance of approx. 40 mm, the resulting geometrical blurring was in the same order of magnitude (100 µm). In the horizontal direction, the field of view was reduced to 100 pixels (62.5 µm) to increase the read out rate and avoid the collection of unnecessary data. For *in-plane* imaging, the anisotropic resolution enhancement methods developed at PSI were applied. A scintillator screen made of Gd₂O₂S with a thickness of 10 µm was positioned behind the cell at an angle of 5.8° with respect to the beam axis, resulting in a magnification factor of approximately 10 in the horizontal direction. The resulting pixel size was 6.2 µm in the horizontal direction and 61 µm in the vertical direction, and the measured effective resolutions (10% MTF half period) were 12 µm (horizontal) and 140 µm (vertical). In this case, an anisotropic collimation was used with a horizontal L/D ratio of 1000 and a vertical L/D ratio of 100. With a sample-detector distance of 25 mm, this translated into a geometrical blurring of 25 µm (horizontal) and 250 µm (vertical), which constitutes the major resolution limitation in this case.

### 7.3.5 Image processing

The image processing consisted of a correction of the detector background, a 3D median filter of 3x3x3 pixels (x, y, t), a flat field correction, a correction of the background due to neutrons scattered by the setup and a correction of beam intensity fluctuations and cell displacements. Subsequently, the images were referenced pixel-wise to their radiograms in the dry state. The thickness of water δ was calculated according to the Lambert-Beer law:

\[
\frac{I}{I_0} = e^{-\Sigma \cdot \delta}
\]  

(7.1)

where \(I\) represents the intensity of the image of the operating cell, \(I_0\) the intensity of the dry reference, and \(\Sigma\) the macroscopic cross-section of water, known to be 5 cm⁻¹ for the *through-plane* setup and 4.5 cm⁻¹ for the *in-plane* setup. Further details about the image processing can be found in Ref.[103]. In a previous work[104], an *in situ* calibration process using the production of a defined quantity of water was performed, showing the measured water thickness is systematically underestimated in the *in-plane* setup, but show a reasonable repeatability between different cells and different experiments. As a result
of this calibration, the water quantities reported here for the measurements done with the in-plane setup were corrected by a factor 1.53.

7.3.6 Data quantification

An example of images obtained using the through-plane and in-plane configurations are shown in Figure 7.1a. In the through-plane image, the dotted lines indicate the boundary between channel and ribs. The quantification of water was performed separately for the rib and channel regions by calculating the median of all 5 channels and all 4 ribs. 50% of the channel and rib area (the central fraction) were used to minimize transition effects. Median values were preferred to average values to work around the presence of water droplets in the channels, as shown in Figure 7.1b. Therefore, pixel-wise median projections were calculated for each condition.

In the cases where large static droplets were found in more than one channel simultaneously, we did not consider these channels for the calculation of water content in the porous media under the channels. If those blocked channels were used, overestimated values would be obtained. The very same procedure was followed to calculate the attenuation profiles under the ribs, without the problems related to water droplets in this case. In order to obtain the attenuation profile for a given condition, we averaged the profiles obtained for each neutron radiograph over a period of 14 minutes (after waiting 6 minutes for stabilization). The same procedure was employed for the in-plane images. In this case the water droplets are not an issue, as they do not superimpose to any region of interest.

7.4 Results and Discussion

7.4.1 Impact of hydrophilic/hydrophobic pattern

The results of the IV curve experiments for cells without MPLs and operated at 70°C are shown in Figure 7.2a for two different values of cathode relative humidity. It can be seen that at full humidity flooding occurs at rather low current densities. This may be due to the flooding of the CL itself, or to the formation of a layer with high water saturation at the CL/GDL interface\cite{204}, the latter being here the most probable case of poor cell performance as the PGA analysis indicates bulk diffusion limitations as the main source of losses (Figure 7.2b). This poor performance at high humidity is a characteristic behavior of cells lacking an MPL\cite{15,16}. At RHca=30\%, the power density obtained is fairly high and cells with patterned wettability exhibit superior performance at high current densities (i>1.0 A·cm\(^{-2}\)). At 1.75 A cm\(^{-2}\), for example, cells in the baseline
configuration show about 150 mV higher bulk diffusion losses compared to those containing modified GDLs, while no notable differences were measured between both types of patterns. At RH_{ca}=100\%, severe flooding occurs at i>0.4 A\cdot cm^{-2} (Figure 2a), which is followed by a stiff increase of bulk losses (Figure 7.2.b). Again, the cells containing GDLs with patterned wettability showed reduced bulk losses under this condition. A possible explanation is that the hydrophilic regions remove the dense water layer mentioned above from at least part of the hydrophobic domains. This new water segregation leads to increased oxygen diffusivity, as reported previously\[^{69}\]. The cells having the narrowest pattern (250-1000 μm) exhibit the best performance in this case. To understand this, we can consider that without a MPL, the CL below the hydrophilic lines has very poor oxygen supply and can be considered as an inactive region. The lower hydrophilic fraction of the narrow pattern makes this issue less important than for the wide pattern. At 50°C, very similar trends are observed (see Appendix A, Figure 7.11).

![Figure 7.2 - Polarization curves at two different values of RH_{ca} (30 and 100\%) for three cells having different cathodic GDLs (baselines, patterned 500 and patterned 250) without MPLs. (a) η curves; (b) bulk losses vs i. The operating temperature was 70°C.](image-url)
In order to explain the differences observed in performance, neutron radiographs are shown in Figure 7.3 at two selected conditions. The data points have been chosen where pronounced performance differences were observed between baseline and modified materials.

Figure 7.3 - Through-plane neutron radiographs for three cells (without MPL) containing different cathodic GDLs (Baseline, Patterned 500 and Patterned 250) are shown for two different conditions: (a) 1.75 A cm\(^{-2}\), RH\(_{an}\)/RH\(_{ca}\) = 100/30%; (b) 0.50 A cm\(^{-2}\), RH\(_{an}\)/RH\(_{ca}\) = 100/100%; Water profiles are shown at the bottom for the same images differentiating between rib and channel area.

It can be seen that the cell containing untreated GDLs shows a rather homogenous profile of water (with an average water content of \(~70\ \mu m\)). At RH\(_{ca}\)=30% and \(i=1.75\) A cm\(^{-2}\) (Figure 7.3.a), a clear water accumulation under the ribs of the hydrophilic domains is obtained for the cell containing the widest pattern (Patterned 500). A water
thickness of ~90 µm and ~30 µm is measured on the hydrophilic and hydrophobic regions, respectively. A less clearly defined water structuring (~80 µm in the hydrophilic and ~60 µm at the hydrophobic) is obtained for the cell containing the narrowest pattern (Patterned 250). Under this condition, the water content under the channels is rather low for every cell; however the baseline shows slightly higher water amounts under the channels.

At higher cathodic relative humidity ($\text{RH}_{\text{ca}}=100\%$, $i=0.50 \text{ A cm}^{-2}$) a similar water distribution was observed (Figure 7.3.b). Under the ribs, the water structuring appears more clearly in the case of Patterned 500 (~130 µm in the hydrophilic and ~60 µm in the hydrophobic region) and surprisingly no clear water segregation is visible in the Patterned 250. Higher water contents are measured under the channel region for the baseline, which indicates a better water removal from the GDL to the gases in the flow channels.

The fact that poor water segregation is obtained using narrow patterns could be explained by the limitations in water transport due to insufficient pore connectivity, as discussed in detail in our previous work [157]. The capillary pressure characteristics reported in this previous work cannot alone explain the liquid water distribution in an operating cell, because the aspects of evaporation and transport in vapor phase are not included in such room temperature experiments. Nevertheless, capillary flow is still an important component of water transport at 70°C as long as liquid water is present. Interestingly, fuel cell performance is still superior. It is worth mentioning that the attenuation signal measured in the through-plane neutron radiographs includes a superposition of both GDLs (anodic and cathodic), as well as the CL-GDL interfaces of both half-cells.

Figure 4 shows the water distribution in a cell having modified GDLs in the cathode at low $\text{RH}_{\text{ca}}$. These results provide information about how the electrochemically produced water is transported in the fuel cell, since the water content in the gas stream is very low. Up to ~ 1.0 A cm$^{-2}$, the water content under the ribs remains very low, probably due to sufficient gas phase transport and effective removal. At 1.0 A cm$^{-2}$, a flat water profile (~ 25 µm water) is measured and the next data point ($i=1.25 \text{ A cm}^{-2}$) already reveals a preferential filling of the hydrophilic domains. The water produced electrochemically in the cathodic CL first fills the CL-GDL interface rather homogeneously up to a point in which the built-up capillary pressure is sufficiently high to produce liquid water breakthrough. From the radiographs it can be seen that the hydrophilic regions fill preferentially due to a lower contact angle and therefore a lower pressure is required to fill those pores. The following points show a further increase of water content in the
In situ characterization

hydrophilic domains (up to ~90 μm of water) while the water content in the hydrophobic regions remains nearly constant (~30 μm of water). Once breakthrough has occurred in the hydrophilic regions, the water produced in the CL finds a low capillary pressure pathway throughout these regions, therefore progressively increasing the water content up to complete saturation.

Figure 7.4 - Through-plane neutron radiographs of Patterned 500 cell for different current densities (1.0, 1.25, 1.50 and 1.75 A cm$^{-2}$) at RH$_{in}$/RH$_{out} = 100/30\%$. Water thickness versus cell position profiles are plotted in the bottom graph for various increasing current densities under the rib area. The profiles under the channel area showed very low water content for every current density.
7.4.2 Influence of adding a microporous layer

Compared to the polarization curves previously discussed (Figure 7.2), the addition of microporous layers significantly improves the performance for low and high gas humidity (Figure 7.5).

![Polarization curves at two different values of RH\textsubscript{ca} (30 and 100%) for three cells having different cathodic GDLs (baselines, patterned 500 and patterned 250) with MPLs. (a) IV curves; (b) bulk losses vs \( i \). The operating temperature was 70°C.](image)

For example, at RH\textsubscript{ca} = 30\% and 1.5 A cm\(^{-2}\) only 50 mV (Figure 7.2.b) of bulk losses are measured when MPLs are used (for every cell), while 150, 80 and 75 mV (Baseline, Patterned 500 and Patterned 250) were measured for the cells lacking MPLs (Figure 7.3). At higher current densities, superior performances using our modified GDLs were measured. As previously, the difference can clearly be attributed to bulk diffusion limitations, as indicated by the results of the PGA method (Figure 7.5.b). At 2.0 A cm\(^{-2}\), the baseline cell shows ~100mV (Baseline+MPL) higher bulk losses vs. the cells with
patterned wettability (Patterned 500+MPL and Patterned 250+MPL). For these operating conditions, the water distribution can be seen in Figure 6a. The cell exhibiting the best performance (Patterned 500) shows a clearly defined water pattern with preferential accumulation in the hydrophilic regions under the ribs. As previously observed, the narrowest pattern is not clearly defined – but still shows increased performance. The water content under the channels is very low in every case.

At RH_{ca}=100% a similar trend is seen: cells containing modified GDLs only flood at higher current densities and with reduced bulk losses at i>0.5 A cm\(^{-2}\) vs. the baseline. For example, at i=1.0 A cm\(^{-2}\), the bulk losses are ~270mV (baseline), ~75mV (patterned 500) and ~100 mV (patterned 250). Under this condition, the through-plane neutron radiographs (Figure 7.5.b) show that water distribution is very similar as discussed in the previous paragraph (Figure 7.5.a), however higher total amounts are obtained. The measurement of water under the channels was not extracted in this case due to static water droplets being present. Interestingly, water droplets seem to be produced at the channel in the adjacent region of the hydrophilic patterns (Figure 7.5.b, Patterned 500), thus showing the capacity of the hydrophilic patterns to transport laterally the water to these locations.

Let us compare the water distribution of cells with and without MPLs (Figure 7.3 and Figure 7.6). Even if the operating condition is not the exact same for the two cases, it seems clear that the preferential accumulation of water in hydrophilic regions is less pronounced for the case with MPL than for the case without MPL. An example comparing water distribution of cells with and without MPLs under the same condition can be found in the Supplementary Information (Appendix A, Figure 7.12). This can be explained by the differences in the way the water is injected into the GDL\(^{[26]}\). When MPLs are used, their inhomogeneities (i.e. cracks, holes or simply the pathways resulting in the smallest capillary barrier) mostly determine the point where water will get through, as the capillary pressures in the MPL is 1-2 orders of magnitude higher than in the GDL. This injection mode increases the probability of water being forced through the hydrophobic regions, therefore reducing the water segregation. On the contrary, when no MPLs are used and CL and GDLs are directly in contact, the water produced electrochemically all over the active area can be easily transported to the hydrophilic regions creating continuous water removal pathways of low capillary pressure.
In situ characterization

Figure 7.6 - Through-plane neutron radiographs for three cells (with MPL) containing different cathodic GDLs (baseline, patterned 500 and patterned 250) are shown at the top at two different conditions: (a) 2.0 A cm$^{-2}$, RH$_{an}$/RH$_{ca}$ = 100/30%; (b) 1.0 A cm$^{-2}$, RH$_{an}$/RH$_{ca}$ = 100/100%; Water profiles are shown at the bottom for the same images differentiating between rib and channel area.

7.4.3 Influence of cathode relative humidity

Figure 7.7 presents a comparison of the cells’ response to various cathodic relative humidities (at a fixed current density). Operation at two temperatures (50 and 70°C) and cells with and without MPL are compared. The various indicators for performance losses (bulk, non-bulk and ohmic losses) are presented for each cell and condition. At 50°C, the cell with no MPL suffers severe voltage loss at RH$_{ca}$>40%, indicating cathode flooding (Figure 7.7.a). This effect is minimized by incorporating MPLs on both anode and cathode. In both cases with and without MPLs, the cells containing GDLs with patterned wettability exhibited significantly superior performance, in particular at high
In situ characterization

cathodic humidity. The same trends are observed at 70°C (Figure 7.7.e). However, at this temperature, the performance differences between baselines and cells containing modified materials are significantly reduced when using MPLs. In every case, the cells containing GDLs with patterned wettability in the cathode presented superior performance at high cathodic gas RH.

The bulk-losses indicator shows that significant differences exist between cells with patterned wettability and baselines for every case. At 50°C (Figure 7.7.b), 100% RH and 0.75 A cm\(^{-2}\) (with MPL), cells with patterned wettability have about 45 mV bulk-losses, much lower than the 220 mV measured for baselines. A similar effect is observed at 70°C, though it is less pronounced when including an MPL (Figure 7.2.f). From the analysis of the different performance loss contributions, it seems clear that bulk-losses dominate the differences observed between cells containing GDLs with patterned wettability and baselines, pointing out diffusion through the GDL as the mechanism responsible for these differences.

The non-bulk losses indicator shows only little variations over the complete range of RH\(_{ca}\). Interestingly, at 50°C significant differences were observed for samples having MPLs (Figure 7.7.e), with a value of approximately 20 mV, and cells having no MPL, for which this value is about double (≈50 mV), although the RH series was measured at a lower current density. The accumulation of liquid water in the CL – as mentioned in our previous work following similar observations\[^{[204]}\] – could explain the higher values of non-bulk losses. At 70°C (Figure 7.7.g) this effect seems to disappear and rather similar non-bulk losses are obtained in both configurations (with and without MPLs). In general, for both temperatures, for the whole humidity range and regardless of the presence of an MPL, no significant differences are observed in terms of non-bulk losses between the baselines and the cells containing GDLs with patterned wettability.

The ohmic losses (Figures 7.7.d and 7.7.h) show, as expected, a dependence on relative humidity which is particularly visible in the case without MPL and at 70°C. At 50°C, the cells seem to be well humidified already at the lowest value of RH\(_{ca}\), which is consistent with the lowest saturation pressure of water vapor at this temperature. When using an MPL, no impact of using a GDL with patterned wettability can be seen. On the contrary, the cells without MPL show higher ohmic losses for the GDLs with patterned wettability than for baselines. This effect represents a difference of 8-10 mV at 0.75 A cm\(^{-2}\), equivalent to a difference of resistivity of 10-13 mΩ cm\(^2\). This difference is independent of the temperature and the humidity, suggesting differences in GDL conductivity or in the contact resistance, the latter being more probable as differences in GDL conductivity would affect the cases with MPL as well. The reason why using patterned wettability would increase the contact resistance is not clear and would require
further investigation. With the number of samples investigated, we also cannot exclude that this difference is only coming from the statistical sample-to-sample variation.

**Figure 7.7** - Loss indicators during the RH series experiments for materials with and without MPLs at two operating temperatures.
As observed before (Figure 7.3 and Figure 7.6), the water redistribution seems to be the reason for decreased bulk-losses. Investigating the change in water distribution at increasing RH_{ca} (constant $i=0.75$ A cm$^{-2}$) shows that water begins to accumulate preferentially on the hydrophilic domains at RH_{ca}>60\% (Appendix A, Figure 7.13). Lower values of cathodic humidity do not seem to limit the water removal in the vapor phase.

As explained in the experimental part, in-plane neutron radiographs were taken for selected experimental points. While in the through-plane images the water distribution over the entire cell area with superimposed layers was analyzed, the in-plane images allow for a quantification of the water in each layer separately. Figure 8a shows that water tends to accumulate preferentially under the rib areas of the cathodic GDL. At increased RH_{ca}, the baseline cell happens to contain higher water amounts under the channel areas than the cells with patterned GDLs, especially for the case of Patterned 500 where clearly lower water content is observed under the channel areas. Not surprisingly, this is the cell showing the best performance (lower bulk mass transport losses) at high RH_{ca}. Some anodic channels contain water droplets in the Baseline case; however, we would not expect this water to have a significant impact on performance.

A systematic analysis of the average water thickness was carried out for the cathodic GDL of each cell (Figure 7.8.b). The regions selected correspond to half of the GDL thickness which is closer to the MPL (and therefore CL) – Region 1- and the remaining half thickness which is closer to the flow field channels – Region 2- (Figure 7.8.c). Region 1 contains higher water amounts than region 2, both under the ribs and channel areas. This observation is not surprising since that region is closer to the water producing interface and further from the gas uptake locations.

An analysis on region 1 (Figure 7.8.b) shows that the water amounts under the ribs are quite similar ($\sim1.05$ mm) for Baseline+MPL and Patterned 500+MPL and slightly higher for Patterned 250 ($\sim1.20$ mm). This proves that the total water amount is similar in all the cells; however the distribution is completely different as previously seen in the TP radiographs (Figure 7.6). The water thicknesses extracted from region 2 (Figure 7.8.b) show that the water content is rather similar under the ribs for every cell over a wide range of RH_{ca}. Surprisingly the baseline cell shows much higher water content ($\sim0.8$ mm) under the channel areas compared to the cells with modified GDLs ($\sim0.3$-0.4 mm). This could be explained by a more efficient way to remove the water under the channel region thanks to the presence of hydrophilic domains. After the formation of the water pathways throughout the hydrophilic domains, continuous water clusters serve as low-energy removal pathways which minimize the water content in the hydrophobic regions.
Figure 7.8 - In-plane neutron radiography results of RH series experiments. (a) Radiographs of three cells (Baseline, Patterned 500+MPL and Patterned 250+MPL) at three RH$_{ca}$ (40, 80 and 100%). (b) Water thickness under versus RH$_{ca}$ ribs and channels at two different cathodic GDL locations. (c) Detail of cathode GDL showing the two regions used for quantification.
Droplets form in the channels around the hydrophilic domains (Figure 7.6) and the removal of droplets by evaporation or simply gas flushing displaces a new portion of water from the CL-MPL-GDL interfaces. Even if 1/3 of the area under the rib (Patterned 500+MPL) is sacrificed (assuming full saturation of the GDL on the hydrophilic domains), this configuration is more convenient for the water removal than homogeneously treated materials (Baseline+MPL).

7.4.4 Effect of temperature on water distribution

In this section the influence of temperature on the water distribution in operating cells is briefly discussed. The electrochemical data discussed in previous paragraphs (IV polarization curves and RH series) demonstrated that the cells containing modified GDLs in the cathode side perform better than those without patterned wettability. These effects were as well observed when operating the cells at lower temperature (50°C). However, as logically expected, the power densities obtained are significantly lower than those measured at 70°C. The influence of temperature has been extensively studied in the literature and the higher amount of liquid water at lower temperatures limits notably the performance at high current densities[205, 206].

![Neutron radiographs showing the water distribution at two cell temperatures (50 and 70°C) and RH_{ca} (30% and 100%) for a cell construction without MPL (Patterned 500) and at 0.75 A cm^{-2}.](image)

In Figure 7.9, neutron radiographs at two different cell temperatures and RH_{ca} (same current density) are shown. For a given condition (i.e. 0.75 A cm^{-2}, 30% RH_{ca}), it is clear that significantly higher liquid water amounts are present at 50°C and that water occupies the hydrophilic regions under the ribs, while at 70°C rather high liquid water
content exists. The channels areas are almost free of water, probably due to virtually unlimited water uptake by the cathode gas. When feeding fully humidified cathode gas (0.75 A cm\(^{-2}\), 100% RH\(_{ca}\)), the cell operated at 70°C shows very sharply defined liquid water domains under the ribs at the hydrophilic domains and, to a lesser extent, under the channel areas. Interestingly, the cell operated at 50°C showed very well defined water patterns in both rib and channel areas. These differences highlight the importance of not only capillary transport, but also evaporation and condensation processes within the cell. At lower temperatures, evaporation rates are notably reduced and therefore water patterning can be observed as well under the channel regions.

7.4.5 Improvements in power density

The last part addresses the achieved improvements in cell power density under various conditions (Figure 7.10). Using GDLs with patterned wettability at the cathode, the fuel cell performance was improved in every case with respect to the use of unmodified materials (baselines). Cells without MPL deliver power densities (at 0.60V) of ~0.76 W cm\(^{-2}\) (~8% improvement) at low RH\(_{ca}\) and dramatically lower at full RH\(_{ca}\). The best results were obtained with the cell containing the narrowest pattern which still provided ~0.54 W cm\(^{-2}\) at full humidity.

![Figure 7.10](image.png)

**Figure 7.10** - Power density (at 0.6V) of cells containing different cathodic GDLs, with and w/o MPL and at two different RH\(_{ca}\). The operating temperature was 70°C.
The addition of a self-standing MPL permitted notably increasing the power density by reducing the electrode flooding as seen in the in-plane neutron radiography measurements. At RHₐ=30%, power densities of ~0.99 W cm⁻² were obtained for cells containing GDLs with patterned wettability (~9% improvement). At full relative humidity these differences became more notable, reaching power densities for cells with the widest pattern (500-930 µm) of ~0.66 W cm⁻² (~33% improvement).

7.5 Conclusions

We have demonstrated that the use of modified gas diffusion layers (GDLs) with patterned wettability for PEFCs results in improved operando performances. The major conclusions of the present study are:

- Imaging the water distribution in an operating cell shows that, as expected, water preferentially accumulates in the hydrophilic patterns. This is much more clearly defined for the wider pattern (500 µm).
- The addition of a microporous layer significantly impacts water distribution by reducing the differences in water content between hydrophilic and hydrophobic regions. The fact that water injection from MPL to GDL is mostly determined by the MPL imperfections could explain these differences.
- The *operando* performance (power density) has been significantly improved in a wide range of operating conditions and cell configurations. These results show the potential of these materials to optimize water management in PEFCs.
7.6 Appendix A – Supplementary material

7.6.1 Section S1: IV curves at 50°C (without microporous layers)

Figure 7.11 - Polarization curves at two different values of RH in (30 and 100%) for three cells having different cathodic GDLs (baselines, patterned 500 and patterned 250) without MPLs. (a) IV curves; (b) bulk losses vs i. The operating temperature was 50°C.
7.6.2 Section S2: Comparison of water distribution at a given condition with and w/o MPL for Patterned 500

Figure 7.12 - Water thickness versus cell position at 0.75 A cm$^2$, full humidity conditions ($\text{RH}_{\text{in}}/\text{RH}_{\text{ex}}=100/100\%$) and 70°C. Two cells are compared: Patterned 500 (w/o MPLs) and Patterned 500 + MPLs.
7.6.3 Section S3: Water distribution at increasing RH$_{ca}$ for Patterned 500

Figure 7.13 - Through-plane neutron radiographs of Patterned 500 cell at 0.75 A cm$^{-2}$ at various RH$_{ca}$ are shown on top. Water thickness (under the ribs) versus cell position curves are shown at the bottom.
Chapter 8. Conclusions and outlook

In the closing chapter, the main conclusions of this PhD thesis work are enumerated. Summaries have been organized in four subsections according to the principal mainstreams of this study. Finally, a suggestion for future work based on durability, optimized fuel cell performance and scalability is provided.
Conclusions and outlook

8.1 Summaries

In the following paragraphs the main learnings will be summarized. For the sake of clarity, the contents have been divided in four subsections.

8.1.1 Radiation grafting of GDLs

Initial parametric studies performed using flat systems allowed finding synthetic conditions to produce hydrophilic surfaces using short reaction times (i.e. 10-30 min). Two monomer systems were evaluated (AA and NVF) and it was proven that while AA tends to graft throughout the polymer bulk, NVF grafts towards external surfaces. A combination of external wettability measurements with FTIR confirmed these trends.

The knowledge obtained for flat system was successfully translated to porous GDLs. While the synthesis of GDLs with NVF was straightforward as the monomer readily wets the GDL, the use of water-based solution of acrylic acid required a special reactor design to provide vacuum. Coating loads of, at least, 15%wt. FEP were needed in order to provide spontaneously wicking materials. Due to the rough nature of the GDL surface, droplets held on its surface define an apparent contact angle, which is generally greater than the intrinsic contact angle. We correlated the measured apparent contact angle with the estimated intrinsic contact angle in the light of the Cassie-Baxter theory.

A preliminary study on thermal stability showed that exposing the treated GDLs to elevated temperatures (i.e. 270°C which is the polymer sintering temperature) would lead to notable degradation and loss of hydrophilicity. From the FEP-g-pAA system, the formation of the sodium acrylate salt minimized this effect.

8.1.2 Electron beam optimization

A study combining experiments with Monte Carlo simulations was performed with the objective of producing high resolution patterns in thick porous materials. It was learnt that the absorbed dose distributes notably around the areas adjacent to the “region of interest” leading to a resolution loss in the range of \( E = 140-200 \text{ keV} \). Interestingly, at slightly higher electron energies (~300 keV), this effect disappears and much greater resolution can be achieved.

Further, it was found that the spacing between mask and substrates has an important influence in the achievable resolution, especially at lower energies. The backscattered electrons from materials below the substrate was found to have a negative effect if high atomic weight materials (i.e. steel) were used. It was proven that a bi-layered material, such as a GDL-MPL, can be selectively modified only throughout the selected layer.
8.1.3 Capillary pressure characteristic

From the *ex situ* capillary pressure characterization, it was learnt that GDL materials having more regular structures, namely narrower pore size distribution and smaller average pore diameter, lead to a better water segregations. The GDL coating load also has a notable influence, being 30% wt. FEP needed to provide good water segregation. Interestingly, it was found that narrower patterns provide poorer segregation than wider patterns. As logically expected, grafting NVF provided better quality segregation than grafting AA, due a superior hydrophilicity. Finally, a comparison between mono-channel and homogeneous injection showed that lateral transport (in-plane) shifts capillary pressure to higher values.

8.1.4 In situ performance

As a closing part, a selection of promising modified GDLs was tested on the cathode side of operando fuel cells. It was shown that, under various temperatures and gas humidities, the fuel cell performance was significantly improved, especially at high current densities when mass transport becomes relevant. This in situ study was performed in combination with the PGA method and neutron imaging. From the PGA we learnt that the bulk mass transport losses are significantly decreased when using modified GDLs and that ohmic and non-bulk losses are not influenced. From the neutron radiographs it was demonstrated that water redistributes according to the pre-designed pattern and that water preferentially accumulates in the hydrophilic domains.

8.2 Conclusions

To the best of the author's knowledge, the development of GDLs with patterned wettability is the first work published in scientific literature involving covalent-bond chemical modification of the polymeric coating. On top of this, the radiation grafting method brings significant advantages to the previously reported approaches in terms of material performance and scalability potential.

Very good quality of hydrophilic-hydrophobic patterns has been obtained using the electron radiation grafting method, as proven by *ex situ* characterization methods, named elemental mappings and capillary pressure characteristics. Finally, it has been demonstrated that fuel cell performance is improved under various operating conditions thanks to an advanced water management.

This original work on development of GDLs with patterned wettability should serve mainly as: (I) proof-of-concept that chemically modified GDLs can be used on the
cathode to improve performance; (II) set a basis and practical guidelines to synthesize porous materials with patterned wettability which may motivate further research in the field.

8.3 Outlook

Suggestions for future work are divided in four areas described below.

8.3.1 Durability

An important aspect is related to the long-term durability of the modified GDLs. In standard GDLs the two main structural components, carbon fibers and hydrophobic coating, are highly stable materials. By forming hydrophilic copolymers between coating and grafted molecules, two questions need to be addressed in the future:

- \textit{How stable is the grafted copolymer under relevant fuel cell operating conditions?} The water leaving the fuel cell is acidic and some metal ions are present. Degradation could occur leading to detachment of grafted groups and potential hydrophilicity loss.
- \textit{How are the newly grafted compounds affecting other fuel cell components?} The presence of new molecules, which could eventually undergo chain scission, could have some impact in catalyst layers or membrane.

Once these aspects are better understood, a next step would require the long term operation of fuel cells devices (>5000 hours) under relevant operating conditions.

8.3.2 Cathode application – MPL

The most straightforward application of GDLs with patterned wettability is to use them in the cathode side of PEFCs with the objective of reducing mass transport losses by providing optimized liquid/gas transport characteristics. In this dissertation, efforts have been done pursuing this goal. The use of MPLs is crucial to obtain high power densities, especially under high relative humidity conditions. In this work, self-standing MPLs were used to gain a preliminary understanding on their influence in water transport and performance in combination with GDLs with patterned wettability.

Future work should include the application of MPLs which are incorporated (embedded) into the GDL. The various available coating methods (spray, doctor blade, etc.) and ink formulations may be considered in the search of optimal combination of MPLs with modified GDLs. In this context, an important issue relates to the possibility of also grafting the MPLs. Finally, special attention should be paid to the thermal
treatments used when incorporating MPLs (solvent evaporation, sintering, etc.) since they can notably impact the grafted polymers, as preliminarily shown in Chapter 4.

8.3.3 Application to evaporative cooling

Apart from the application of modified GDLs on the cathode side, a novel application is under development in our laboratories. In this case, modified GDLs with engineered superhydrophilic channels are used in an evaporatively cooled fuel cell. Liquid water is fed to the cell, wicked by the GDL and evaporated to cool down the cell. Very promising preliminary results have been obtained by Cochet et al. [207].

8.3.4 Scaling-up

In the frame of this work, a patent application has been filled and has received a very positive review. The patent covers all aspects related to the synthesis of GDLs with patterned wettability and their application in evaporatively cooled fuel cells. An important aspect is, therefore, to further develop synthetic steps facilitating the scale-up. The most promising manufacturing concept is the continuous roll-to-toll process. In this context, shorter reaction times would lead to reduced reactor size and facilitate matching process speed with other manufacturing steps. From the technical standpoint, performing the reactions under air (or under some oxygen traces) would also reduce complexity, so research in this direction should be carried out. Finally, the potential of monomers re-utilization needs to be studied, as important cost lowering can be achieved.
Bibliography


## Symbols, Indices and Abbreviations

### Symbols

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<td>$R_P$</td>
<td>Average pore radius (Washburn)</td>
<td></td>
<td>[µm]</td>
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## Constants

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value</th>
<th>Units</th>
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<tbody>
<tr>
<td>F</td>
<td>Faraday constant</td>
<td>96 485</td>
<td>[A·s·mol$^{-1}$]</td>
</tr>
<tr>
<td>R</td>
<td>Universal gas constant</td>
<td>8.314</td>
<td>[J·mol$^{-1}$·K$^{-1}$]</td>
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Symbols, Indices and Abbreviations

Indices

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>()</td>
<td>Cathodic direction (reduction)</td>
</tr>
<tr>
<td>()*</td>
<td>Reference</td>
</tr>
<tr>
<td>()+</td>
<td>Anodic direction (oxidation)</td>
</tr>
<tr>
<td>()°</td>
<td>Standard</td>
</tr>
<tr>
<td>()₀</td>
<td>Initial</td>
</tr>
<tr>
<td>()ₘₐₜₜ</td>
<td>Absorbed</td>
</tr>
<tr>
<td>()ₐₙ</td>
<td>Anodic</td>
</tr>
<tr>
<td>()ₐₚₜ</td>
<td>Apparent</td>
</tr>
<tr>
<td>()₃ₜₜₜ</td>
<td>Refers to bulk losses</td>
</tr>
<tr>
<td>()ₖₖₖ</td>
<td>Capillary</td>
</tr>
<tr>
<td>()ₙₙₙ</td>
<td>Cathodic</td>
</tr>
<tr>
<td>()ₜₜₜ</td>
<td>Charge transfer</td>
</tr>
<tr>
<td>()ₐₑₑ</td>
<td>Effective</td>
</tr>
<tr>
<td>()ₜₜ</td>
<td>Final</td>
</tr>
<tr>
<td>()ₙₚₚ</td>
<td>Fuel cell</td>
</tr>
<tr>
<td>()ₙₙ</td>
<td>Gas</td>
</tr>
<tr>
<td>()ₙₙₙ</td>
<td>Hydrogen</td>
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<tr>
<td>()ₙₙₙ</td>
<td>Water</td>
</tr>
<tr>
<td>()ₙₙₙ</td>
<td>Helox</td>
</tr>
<tr>
<td>()ₙₙₙ</td>
<td>Specie i</td>
</tr>
<tr>
<td>()ₙₙₙ</td>
<td>i≠0</td>
</tr>
<tr>
<td>()ₙₙₙ</td>
<td>Intrinsic or internal</td>
</tr>
<tr>
<td>()ₙₙₙ</td>
<td>Liquid</td>
</tr>
<tr>
<td>()ₙₙₙ</td>
<td>Liquid-gas</td>
</tr>
<tr>
<td>()ₙₙₙ</td>
<td>Limiting</td>
</tr>
<tr>
<td>()ₙₙₙ</td>
<td>Limiting</td>
</tr>
<tr>
<td>()ₙₙₙ</td>
<td>Maximum constriction</td>
</tr>
<tr>
<td>()ₙₙₙ</td>
<td>Minimum constriction</td>
</tr>
<tr>
<td>()ₙₙₙ</td>
<td>Mass transport</td>
</tr>
<tr>
<td>()ₙₙₙ</td>
<td>Mask-to-sample</td>
</tr>
<tr>
<td>()ₙₙₙ</td>
<td>Refers to non-bulk losses</td>
</tr>
<tr>
<td>()₂₂₂</td>
<td>Oxygen</td>
</tr>
</tbody>
</table>
Symbols, Indices and Abbreviations

(\(\cdot\)_\(r\)) Reaction
(\(\cdot\)_\(rel\)) Relative
(\(\cdot\)_\(rev\)) Reversible
(\(\cdot\)_\(S\)) Surface
(\(\cdot\)_\(sb\)) Sample-to-“backscattering material”
(\(\cdot\)_\(SG\)) Solid-gas
(\(\cdot\)_\(SL\)) Solid-liquid
(\(\cdot\)_\(th\)) Thermo-neutral
(\(\cdot\)_\(tot\)) Total
(\(\cdot\)_\(void\)) Void
(\(\cdot\)_\(Ω\)) Ohmic

Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>AA</td>
<td>Acrylic acid</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflectance</td>
</tr>
<tr>
<td>BE</td>
<td>Binding energy</td>
</tr>
<tr>
<td>BP</td>
<td>Bipolar plates</td>
</tr>
<tr>
<td>CA</td>
<td>Contact angle</td>
</tr>
<tr>
<td>CCD</td>
<td>Charged coupled device as image sensor for camera</td>
</tr>
<tr>
<td>CCM</td>
<td>Catalyst coated membrane</td>
</tr>
<tr>
<td>CL</td>
<td>Catalyst layer</td>
</tr>
<tr>
<td>EBL</td>
<td>Electron beam lithography</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>FEP</td>
<td>Fluorinated ethylene propylene</td>
</tr>
<tr>
<td>FEP-g-pAA</td>
<td>Fluorinated ethylene propylene grafted with poly(acrylic acid)</td>
</tr>
<tr>
<td>FEP-g-pNVF</td>
<td>Fluorinated ethylene propylene grafted with poly(N-vinylformamide)</td>
</tr>
<tr>
<td>FFP</td>
<td>Flow field plates</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>Acronym</td>
<td>Abbreviation</td>
</tr>
<tr>
<td>---------</td>
<td>--------------</td>
</tr>
<tr>
<td>GDL</td>
<td>Gas diffusion layer</td>
</tr>
<tr>
<td>HOR</td>
<td>Hydrogen oxidation reaction</td>
</tr>
<tr>
<td>ICON</td>
<td>Beamline for Imaging with COld Neutrons</td>
</tr>
<tr>
<td>LBM</td>
<td>Lattice Boltzmann Method</td>
</tr>
<tr>
<td>MEA</td>
<td>Membrane electrode assembly</td>
</tr>
<tr>
<td>MEHQ</td>
<td>4-Methoxyphenol</td>
</tr>
<tr>
<td>MPL</td>
<td>Microporous layer</td>
</tr>
<tr>
<td>MSP</td>
<td>Method of standard porosimetry</td>
</tr>
<tr>
<td>NR</td>
<td>Neutron radiography</td>
</tr>
<tr>
<td>NVF</td>
<td>N-vinylformamide</td>
</tr>
<tr>
<td>OCV</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PEFC</td>
<td>Polymer electrolyte fuel cell</td>
</tr>
<tr>
<td>PENEOPE</td>
<td>Code for Penetration and ENergy LOss of Positrons and Electrons</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene teraphtalate</td>
</tr>
<tr>
<td>PGA</td>
<td>Pulsed gas analysis</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PNM</td>
<td>Pore Network Modelling</td>
</tr>
<tr>
<td>PSFA</td>
<td>Perfluorosulfonic acid</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polythetrafluoroethylene</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SINQ</td>
<td>Spallation neutron source at PSI</td>
</tr>
<tr>
<td>SLS</td>
<td>Swiss Light Source</td>
</tr>
<tr>
<td>TEMPO</td>
<td>(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermo gravimetric analysis</td>
</tr>
<tr>
<td>TOMCAT</td>
<td>Beamline for Tomographic Microscopy and Coherent rAdiology experimenTs</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>VA</td>
<td>Vinlyamine</td>
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<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<tr>
<td>XTM</td>
<td>X-ray tomographic microscopy</td>
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</table>
Publication List

Peer reviewed publications


**Patent**


**LEC Annual reports**


**Contributed talks**


Posters


Curriculum Vitae

Personal Information

Name              Antoni Forner Cuenca
Place and date of birth  Alicante, December 29th 1989
Citizenship       Spanish

Education

2013-current  Swiss Federal Institute of Technology (ETHZ, Zürich)

2007-2013 University of Alicante (UA, Alicante)
                   Chemical Engineering (B.S.+M.S.) – Master thesis: *Hydrogen production from steam reforming of propane in a heterogeneous catalytic reactor*

2003-2007 Instituto de Educación Secundaria San Blas (IES, Alicante)
                   Secondary education, branch: Technology/Natural sciences

Further education/Professional experience

June 2012- Apr 2013 Technology Trainee Engineer - SABIC Innovative Plastics (Cartagena, Spain)
                   *New catalyst for the diphenyl carbonate (DPC) process: lab and pilot scale evaluation.*

June 2011- Oct 2011 Internship - Center for Applied Energy Research (CAER), University of Kentucky (USA)
                   Projects: *Solar thermal coatings of multiwall carbon nanotubes for parabolic trough collector plants applications and Thermal energy storage materials based on wax infiltrated in carbon foam for medium grade temperature applications.*

June 2010- Sept 2010 Internship - University of Alicante (Spain)
                   *Development of polymer nanocomposites with carbon nanofillers: analysis of the dispersion and mechanical properties*