

Università degli Studi di Padova





MASTER THESIS IN MATERIALS SCIENCE

## Study of the interfacial stability between Proton Exchange Membranes with reduced perfluorinated content and PFSA based catalyst electrodes

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Alla mia famiglia, ed in particolare ad Elisa per la loro presenza, anche da lontano.

To my girlfriend, for brightening every moment, and friends, for sharing the road.

This is the way.

#### Abstract

Fuel cells represent a key technology for the decarbonization of the energy sector as they allow efficient conversion of molecular fuels into electrical energy. Among the fuel cell technologies, Proton Exchange Membrane Fuel Cells (PEM-FCs) are already deployed in the mobility sector due to the high gravimetric and volumetric power density that can be developed by such devices.

However, state-of-the-art solutions for PEMFCs make a widespread use of perfluorinated compounds also known as per- and polyfluoroalkyl substances (PFAS) such as perfluorosulfonic acids (PFSA) and polytetrafluorethylene (PTFE) posing a limitation to the upscaling of this technology due to environmental, health and production cost concerns. Additionally, a ban of PFAS by political regulations within the European Union is more than likely in the near future.

In this work, a fluorine-free proton exchange membrane has been studied with respect to the compatibility with state-of-the-art catalyst layers. The membranes consist of a PE-reinforced blend of sulfonated poly-phenylene sulfones (S-240,  $EW = 240 \ g \ mol^{-1}$ ) and polybenzimidazole (sPPS:PBI-OO). Scope of the study is to assess the compatibility of solid electrolyte and catalysts for Membrane-Electrodes Assemblies (MEAs) with reduced content of perfluorinated compounds. Extremely thin sPPS:PBI-OO membranes (5–10 $\mu$ m) are used to prepare MEAs by means of high-throughput processing technologies. In situ characterizations are performed through polarization curves, galvanostatic EIS, Cyclic Voltammetry (CV) and limiting current measurements.

Afterwards, samples have been characterized by means of Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy and Scanning Electron Microscopy (SEM) to determine aging trends. It was found that S-240 is mobilized under fuel cell operating conditions, causing ionomer wash out and poisoning of the catalyst layer, leading to a 62 % reduction of Electrochemical Surface Area (ECSA) within the cathode catalyst layer and a 55 % increase in limiting current losses related to oxygen diffusion through ionomer layers. Moreover, direct contact of catalyst layer and membrane leads to premature soaking of the fuel cells. However, these membranes displayed advanced performance with respect to the ionic conductivity, with a minimum value of 24.8  $m\Omega cm^2$ . Additionally, a preparation route involving the addition of a Nafion layer between sPPS:PBI-OO membranes and catalyst layers was optimized. This route

allows to stabilize performance during conditioning procedures, prevent catalyst poisoning and reduce water induced gas transport resistance by up to 50 % at 40 °C and 100 % *RH*. A maximum power output of 2.46  $W cm^{-2}$  was achieved while operating in H<sub>2</sub>/O<sub>2</sub> at 80 °C and 100 % *RH* with 2.2 *bar* of backpressure on both electrodes and a gas flow of 2 and 5  $Nl min^{-1}$  for anode and cathode, respectively. This indicates that once fluorine-free mitigation strategies will be developed to prevent sPPS from leaching, good performance will be accessible.

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## List of Acronyms

BMBF German Federal Ministry of Education and Research

ZSW Centre for Solar Energy and Hydrogen Research Baden-Württemberg

MPI Max-Plack-Institut für Festkörperforschung

**CSV** Comma Separated Values

TFC Total Final energy Consumption

**IEA** International Energy Agency

NZE Net Zero Emissions

FCEV Fuel Cell Electric Vehicle

**DOE** Department of Energy

EU European Union

**PEMFC** Polymer Electrolyte Membrane Fuel Cell

**PFSA** perfluorosulfonic acid

PFAS per- and polyfluorinated alkyl substances

HHV Higher Heating Value

LHV Lower Heating Value

GDL Gas Diffusion Layer

MPL Microporous Layer

**CL** Catalyst Layer

I/C Ionomer-to-Carbon ratio

IL interlayer

- **PEM** Proton Exchange Membrane
- **SPE** Solid Polymer Electrolytes
- **BP** Bipolar Plate
- **CCM** Catalyst Coated Membrane
- MEA Memrbane Electrode Assembly
- GDE Gas Diffusion Electrode
- HOR hydrogen oxidation reaction
- HER hydrogen evolution reaction
- **ORR** oxigen reduction reaction
- **OCV** Open Circuit Voltage
- ECM Equivalent Circuit Model
- ASR Area-Specific Resistance
- TLMQ non ideal capacitance Trasmission Line Model
- PE polyethylene
- sPPS sulfonated polyphenylene sulfonate
- sPPPH+ sulfo-phenylated polyphenylenes
- TFE tetrafluoro ethylene
- ETFE Ethylene-Tetrafluorethylene
- PTFE polytetrafluoro ethylene
- ePTFE expanded-polytetrafluoro ethylene
- PBI polybenzimidazole

#### PBI-OO polybenzimidazole

- HC Hydrocarbon
- PE polyethylene
- FER Fluorine Emission Rate
- **IEC** Ionic Exchange Capacity
- RH Relative Humidity
- EW Equivalent Weight
- ECSA Electrochemical Surface Area
- CE counter electrode
- **RE** reference electrode
- WE working electrode
- H<sub>UPD</sub> Hydrogen Underpotential Deposition
- **DLC** Double Layer Current
- HFR High-Frequency Resistance
- LFR Low-Frequency Radius
- AC Alternating Current
- DC Direct Current
- CPE Constant Phase Element
- XRF X-Ray Fluorescence
- CV Cyclic Voltammetry
- LSV Linear Sweep Voltammetry
- EIS Electrochemical Impedance Spectroscopy
- ATR-FTIR Attenuated Total Reflectance-Fourier Transform Infrared

- ATR Attenuated Total Reflectance
- FTIR Fourier Transform Infrared
- SEM Scanning Electron Microscopy
- FE Field-Emission
- EDX Energy-Dispersive X-Ray
- AsB Angular-selective Backscattered-electrons
- SE2 Secondary electrons
- AST Accelerated Stress Test
- AST1 Accelerated Stress-Test 1
- AST2 Accelerated Stress-Test 2
- BoL Begin-of-Life
- EoT End-of-Test
- HD Hot and Dry
- CW Cold and Wet
- Std Standard

# List of Reactions

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# 1 Introduction

In an effort to keep global warming within 1.5 °C, the International Energy Agency (IEA) proposed scenarios that require the accomplishment of Net Zero Emissions NZE by 2050.<sup>[1]</sup> The scenario proposed by IEA (see Fig.1.1) require the use of hydrogen fuel to be applied in all fields whose electrification through batteries is not as advantageous, the so-called hard-to-decarbonise sectors, such as: heavy industries (i.e. steel manufacturing), shipping, heavy-duty road transport and aviation.<sup>[2]</sup>





Additionally, hydrogen can be used to stabilize the power sector by absorb-

ing renewable energy excess to produce hydrogen through electrolysis and be fed back into the energy grid when demand exceeds production. Therefore, hydrogen is expected to play a complementary role to batteries in electrification and to be a facilitator of seasonal energy storage which will become necessary with increasing shares of renewable energy generation.

All the scenarios which consider the use of hydrogen for energy conversion imply the usage of electrolyzers and fuel cells to respectively produce and consume hydrogen. Since in 2021 the emissions from transport accounted for 5.86 Gt  $CO_2^{[3]}$ , the widespread adoption of Fuel Cell Electric Vehicle (FCEV) technology is crucial to accomplish the global warming mitigation efforts. However, fuel cells have not yet reached the growth rate required to meet the diffusion expected by NZE scenarios<sup>[4]</sup>. Indeed, the fleet of FCEVs in 2021 counted only 51,437 units with a marked regionality in distribution, given that 40% of them were sold in South Korea. Furthermore, as Samsun et al.<sup>[4]</sup> referred, 80 % of the FCEV fleet is composed by cars, which is a less effective application compared to heavy-duty transport. This is due to the fact that battery storage systems are less adequate for long-hauling trucks due to excessively short range, high pack weight and long downtime due to recharging.

Public instutitions have appointed technical targets to be met by commercial fuel cells as necessary criteria to achieve competitiveness against thermal engines running on fossil fuels. One of the most prominent entities in this matter is the Department of Energy (DOE) of the United States, which forecasted that the cost of a fuel cell system should converge ultimately to  $30 \ km_{net}$ .<sup>[5]</sup> Given that in 2015 the cost per net power output of a fuel cell system for transportation was  $53 \ km_{net}$ , the ambitiousness of such target can be easily understood. Meeting such severe development requirements is therefore leading the scientific community to experiment with different materials and preparation methods for possible breakthroughs.

Regarding transport purposes, there is general consensus over the use of PEMFC, which is a class of fuel cells characterized by the usage of a polymeric membrane to separate the two electrodes, as described in Section 1.1 for a detailed description of the device and its components. The motivation lies on the fact that this solution can already provide high power density, good durability and can operate at temperatures sufficiently low to be compatible with small scale applications.

## 1.1 PEMFC

A fuel cell is a device used for the electrochemical conversion of chemical energy stored in the form of fuels into electrical energy. Particularly relevant is the possibility to be fuel these devices with hydrogen which can combine with molecular oxygen to form water through the redox Reaction 1.

$$2 H_{2(g)} + O_{2(g)} \longrightarrow 2 H_2 O_{(l)} \qquad \Delta g_r^{\circ} = -237.13 \ kJ \ mol^{-1}$$
 {1}

The reaction is heavily exotermic ( $\Delta H_r^{\circ} = -286.0 \ kJ \ mol^{-1}$ ) and can develop into an explosion if the two reactants get in direct contact. The reaction enthalpy considered involves liquid water formation, also called the Higher Heating Value (HHV). This is more appropriate than the counterpart which considers the production of water vapour (Lower Heating Value (LHV)) for more accurate comparison in efficiencies between heat/expansion engines and fuel cells, since in a conventional combustion device the latent heat coming from water condensation could be recovered.

#### 1.1.1 Behavior at equilibrium

However, the applicative potential of such reaction lies within the possibility to be performed electrochemically by separating the hydrogen oxidation reaction (HOR) at the anode and the oxigen reduction reaction (ORR) at the cathode. If the material separating the electrodes is a proton conductor, the semireactions taking place at the electrodes are as shown in Reactions 2 and 3, respectively. This configuration leads to obtain a potential difference between the two electrodes.

Anode: 
$$H_2 \Longrightarrow 2H^+ + 2e^- \qquad E^\circ = +0.0V$$
 {2}

Cathode: 
$$\frac{1}{2}O_2 + 2H^+ + 2e^- \Longrightarrow H_2O$$
  $E^\circ = +1.229V$  {3}

Potential difference between cathode and anode at equilibrium in standard conditions (25 °C, 1 atm) is derived from the difference in standard potentials of each semireaction  $E_{cell}^{\circ} = E_{cat}^{\circ} - E_{an}^{\circ} = +1.229 V$ . To account for non-standard temperatures, it is necessary to include the reaction entropy in the calculation as reported in Eqn.1.1. 1.1. PEMFC

$$E_T = E^{\circ} - \frac{\Delta s^{\circ}}{2F} \left( T - T^{\circ} \right) = E^{\circ} - \left( 2.298 \times 10^{-4} \, V/K \right) \left( T - T^{\circ} \right) \tag{1.1}$$

Where  $\Delta s^{\circ}$  is the molar reaction entropy, 2 is the number of electrons involved in the electrochemical reaction, *F* is the Faraday constant, *T* is the temperature at which the reaction takes place and *T*° is the standard temperature, which is 25 °*C* or 298 *K*. However, the temperature effect on the thermodynamical potential is rarely appreciable in low temperature devices.

Considering that often the total gas pressure is limited by the design of the fuel cell, much more relevance can assume the partial pressure of reacting gases due to the operation in a wide range of water vapour partial pressures. The functional relationship between the reactant partial pressures and the reversible potential is explicitated by the Nernst equation (see Eqn.1.2).

$$E = E^{\circ} - \frac{RT}{2F} \ln \frac{a_{\rm H_2O}}{p_{\rm H_2} p_{\rm O_2}^{1/2}}$$
(1.2)

Where *R* is the ideal gas constant,  $a_{H_2O}$  is the chemical activity of water and  $p_{H_2}$ ,  $p_{O_2}$  are respectively the hydrogen and oxygen partial pressures.

#### **1.1.2** Behavior out of equilibrium

Whenever the potential difference between the electrodes of an electrochemical cell is different from the thermodynamical equilibrium, the system is said to be in out-of-equilibrium conditions. It is in such out-of-equilibrium conditions that the operation of an electrochemical device takes place. To introduce the principal mechanisms occurring during operation of a PEMFC, the reaction environment must be briefly introduced and a schematic representation is depicted in Figure 1.2.

The cell is characterized by a certain degree of symmetry across the central layer in the functional roles of its components. The outer component is an electronic current collector layer called Bipolar Plate (BP) which features gas inlets and a flow field, the latter being a surface patterned with trenches to establish a continous flow channel between the gas inlet and the gas outlet. An example of flow field can be seen from Fig. 1.3a, which is then assembled with the opposite counterpart to make the whole sample holder as in Fig. 1.3b.

During operation of a fuel cell, the mass flow of gases Q is usually set in relation to the current produced by the PEMFC. A parameter used to express



Figure 1.2: Schematic representation of a single hydrogen PEMFC.



Figure 1.3: (*a*) Picture of a serpentine flow field on a 5 cm  $\times$  5 cm graphite current collector. (*b*) Picture of a sample holder for 25  $cm^2$  single cell testing, assembled with two flow fields having gold plated metal contacts.

this information is  $\lambda$  which expresses the ratio between molar flows fed and consumed by the cell, as reported in Eq. 1.3.

$$\lambda = \frac{\dot{n}_{feed}}{\dot{n}_{consumed}} \tag{1.3}$$

A main engineering issue in fuel cells is to obtain an homogeneous gas flow on the electrocatalyst material while achieving a satisfactory electrical contact with the external circuit.

This problem is tackled by placing layers with decreasing pore size between the current collector and the electrochemically active layers. The state of the art

#### 1.1. PEMFC

approach consist in the use of an outer Gas Diffusion Layer (GDL) with a fibrous texture visible to the naked eye and an inner Microporous Layer (MPL) which has a pore size small enough to be perceived simply as a rough surface. Often these two layers are provided as a single assembly to ease the handling.

The two Catalyst Layers (CLs) are placed in direct contact with the membrane and have the complex role of catalyze the electrochemical reactions while maintaing a sufficient electronic contact with the MPLs as well as ionic contact with the central layer of the device, a PEM. This PEM has the duty to sustain the ionic current between the electrodes while preventing the passage of electronic current as well as isolating the reaction environments by blocking gas crossover. Controlled humidification of a polymeric PEM is fundamental for the correct function of the cell and therefore its effects are detailed in Section 2.1. Finally, single cells are usually piled on top of each other to obtain a *stack* of elements connected in series, capable of generating a high voltage ( $V_{stack}$ ). The relevant conditions to operate for a hydrogen fuel cell are the ones in which the load is lower than the equilibrium potential, in order to promote consumption of the fed gases.

During the operation of a fuel cell, several irreversible loss mechanisms occur and all contribute to an overall overpotential,  $\eta$ , which is defined as the difference between *E*, the thermodynamical potential at the conditions of the cell, and *U*, the load between electrodes.

$$\eta_{tot} = E - U = \eta_k + \eta_{ohm} + \eta_{mt} \tag{1.4}$$

The total loss due to the dynamic conditions can be factored into three distinguished contributions afferring to kinetical ( $\eta_k$ ), ohmic ( $\eta_{ohm}$ ) and mass transport losses ( $\eta_{mt}$ ) as in Eqn.1.4. Accounting for these losses and their dependence on the current density flowing through electrocatalyst and PEM leads to define a realistic performance curve for a PEMFC. For PEMFCs, the usual performance curve is named also polarization or I-V curve, due to the fact that reports the load as a function of the current density. A realistic plot of such curve can be seen in the following Fig. 1.4. As reported in the plot, each kind of overpotential is characterizes the slope of a polarization curve in a separate current range. At low current densities, the logarithmic growth of  $\eta_k$  is clearly visible until it develops in a more linear slope, characteristic of an ohmic regime ( $\eta_{ohm}$ ). Then



Figure 1.4: Example of polarization curve for a PEMFC with  $\eta$  on the second *y*-axis. The regions are delimited to denote where the trend of the curve is dominated by the indicated overpotential contribution.

at high current densities, an asymptote appears due to the fact that  $\eta_{mt}$  diverges as the current density approaches the limit current density.

## **1.2** Study case context

The benchmark material for the realization of PEMs are compounds called PFSAs. These compounds are copolymers of perfluoro(vinyl ether) terminated by a sulfonyl fluoride group and tetrafluoro ethylene (TFE). As presented in Fig 1.5, PFSAs are therefore characterized by a branched polymeric structure with a backbone consisting in a chain of perfluorinated carbon atoms  $(-CF_2-)$  and analogous side chains acidified by a terminal sulfonate group  $-SO_3H$ .

However, their use is being reconsidered as a result of the limitations they pose to the commercialization of PEMFCs due to health and environmental risk, costly synthesis as well as limited operating temperature range.<sup>[6]</sup> Indeed, PFSAs are long-chained PFAS whose toxicity is mainly due to accumulation in living beings possibly affecting the human health in the ways displayed in Table 1.1.<sup>[7,8]</sup>



Figure 1.5: Molecular structure of PFSAs.

Direct exposure	Development effects on unborn child
Thyroid disease	Reduced response to vaccines
Increased cholesterol levels	Lower birth weight
Liver damage	Delayed mammary gland development
Kidney cancer	
Testicular cancer	

Table 1.1: Confirmed effects on the health correlated with PFAS accumulation in the human body. Source:EEA<sup>[7]</sup>

Additionally, PFSA requires expensive synthesis processes to be prepared. Mainly in relation to the need and production of hazardous chemicals, such as hydrogen fluoride, but also due to the number of synthetic steps required to obtain the desired molecular structure.<sup>[9]</sup>

Furthermore, it has become desirable to fuel cell for mobility OEMs to increase the operating temperature above 100 ° C in relation to easier water and heat management<sup>[10]</sup> as well as improved electrochemical performance<sup>[11]</sup> and tolerance to catalyst poisoning<sup>[12]</sup>. Nevertheless, PFSA is negatively affected by high temperatures due to overcoming of its glass transition temperature, which leads to increased gas crossover and loss of mechanical performance.<sup>[13]</sup>

All these details mark the importance of developing alternative membrane materials that can overcome the limitations of PFSA polymers. A particularly promising class of materials that are being studied for this purpose is represented by conjugated hydrocarbons, especially because they are easily sythesized and possess a high degree of versatility in their molecular design, as shown in Fig.1.6.<sup>[6]</sup>



Figure 1.6: Some of the possible structures for hydrocarbon ionomers.

Among the examples presented in the previous figure, only sPPS will be further discussed.

## **1.3** Design of Experiment

It is broadly agreed that tolerance of hydrocarbon membranes to OCV conditions is boosted by the low permeability to gaseous oxygen, which leads to comparatively lower amounts of H<sub>2</sub>O<sub>2</sub> formation at the anode side.<sup>[19]</sup> However, in case of operation at low potential, the release of H<sub>2</sub>O<sub>2</sub> is independent from this property and allows to more evenly compare tolerance to chemical degradation between the polyelectrolytes. Such operating condition is normally achieved in cathode starvation conditioning protocols<sup>[20]</sup>. Moreover, fuel cell operation during cathode starvation leads to frequent and rapid inversion of water transport, accelerating the leaching of soluble or mobilized species from within the membrane. Therefore, careful characterization of prepared fuel cells before, during and after such protocol is the main focus of this study.
# 2 State of the art

This Chapter reports on the state-of-the-art understanding of membrane materials for PEMFCs, providing the literature background necessary to evaluate the different chemistries investigated in this work.

# 2.1 Properties of PEMs

Membranes for the realization of PEMFCs must possess numerous properties in relation to their functions.<sup>[21]</sup> In order to be an eligible candidate, a membrane should firstly possess high performances in terms of high ionic conductivity, low H<sub>2</sub> and O<sub>2</sub> gas crossover as well as a high level electrical insulation of electronic currents. Secondly, chemomechanical stability in a wide range of humidification and temperature conditions is required for the robust operation of a fuel cell. Chemically, a membrane should tolerate the presence of HO  $\cdot$  and HOO  $\cdot$  radicals without degrading as well as not undergo chemical conversions activated by the operation temperature. An example of possible chemical reactions that may take place in polymer electrolytes due to high temperatures is the thermal crosslinking.<sup>[22]</sup> Moreover, membranes must exhibit low levels of swelling and retain a high mechanical stiffness in operative conditions to avoid fracturing and detachments of assembled layers. In this thesis, all membranes used consist in three-layer composites of a porous polymeric reinforcement which is impregnated and covered on both sides by polymer electrolytes, as depticed in Figure 2.1. The use of composite structures is advantageous since it allows to rely on the reinforcement layer for the mechanical properties of the whole membrane,

#### 2.2. WATER STORAGE AND TRANSPORT IN PEMs



Figure 2.1: (a) SEM and (b) EDX sulfur mapping of a composite membrane reinforced with impregnated porous PE wrapped in between polyelectrolyte blends of sPPS and PBI-OO.

allowing to decouple the requirements for electrochemical performance and mechanical stability. Specifically, the ionomer is responsible for electrochemical performance while reinforcement can provide increased mechanical features. This work concentrates on the interfacial stability of hydrocarbon membranes whose chemistry and water storage properties must be detailed to provide sufficient background to experiments and discussions.

# 2.2 WATER STORAGE AND TRANSPORT IN PEMS

Ionic conductivity of proton exchange membranes is attributed to the polymer electrolyte. All the polymer electrolytes treated in this work are characterized by the presence of superacid sulfonate groups, as identified in red within Figure 2.2. These moieties are the reason why PEMs are hygroscopic and therefore possess a degree of hydration in almost any condition. The hydration state is quantified by the hydration number ( $\lambda$ ), a parameter expressing the average amount of water molecules per sulfonate group. Polymer electrolytes can therefore exhibit a great variety of morphologies due the specific interactions between chemical functions within the polymer electrolyte and their respective interactions with water, also depending on the water content. In these materials, morphological structure and water concentration affect indirectly ionic conductivity through the modification of water transport properties and charge



Figure 2.2: Polymer electrolytes studied in this work.

carrier concentration. Indeed, water transport and proton conductivity are mutually influenced by the existence of electro-osmotic drag which correlates the electrical ionic current with a viscous flow of solvent.<sup>[23]</sup> Since the chemical function responsible for ionic conductivity in the treated polymers is the same, their morphology is expected to play a major role in the explanation of their different behavior. In particular, ionomers tend to accumulate water which can be classified into *bound* and *free*, dependint on each molecule's temporary interaction with the polymeric electrolyte.<sup>[24]</sup> Bound water refers to molecules whose dynamic is affected by a chemical or electrostatic interaction with the sulfonate functions, while free water is referring to the molecules which can be considered to not be interacting with such groups and therefore behave as bulk water. This distinction is crucial to water transport properties, since free water being dragged by the protons moved across the membrane will interact with the polyelectrolyte mainly through a viscous flow friction while bound water will be subject to its interaction with a specific sulfonate site and will detach from it through an hopping-based mechanism. The quantitative repartition between viscous and hopping water transport therefore depends on the hydration number, since it determines the amounts of free and bound water present in the polyelectrolyte.

Moreover, a great difference in chemistry between perfluorinated and hydrocarbon polyelectrolytes is reflected in the amount of sulfonate groups achievable. A parameter often used to quantify this property is the IEC, always expressed in millimoles of cations per gram of polyelectrolyte ( $mmol g^{-1}$ ). For PFSA, the IEC is within 0.9 – 1.6  $mmol g^{-1}[25]$ , while polyelectrolytes based on polyphenylene can be designed to have an IEC up to 4.5  $mmol g^{-1}[26]$ . This parameter determines the concentration of charge carriers within the membrane, affecting the

#### 2.2. WATER STORAGE AND TRANSPORT IN PEMs

conductivity arising from hopping mechanism through Eq. 2.1:

$$\sigma = \frac{cF^2D}{RT} \tag{2.1}$$

Where c is the concentration of charge carriers, F is the Faraday's constant, D is the diffusion coefficient, R is the molar gas constant and T is the temperature.

# 2.2.1 PFSA with ePTFE reinforcement

One of the membranes adopted in this study is known commercially as Gore SELECT 765.08 and is characterized by the use of a PFSA ionomer reinforced with expanded-polytetrafluoro ethylene (ePTFE) engineered through the addition of ceria particles. As previously introduced, PFSA represents a state-of-the-art solution for PEMFCs since 1960s.<sup>[9]</sup> A determining feature for PFSA consists in the fundametally dissimilar nature of hydrophilic pendant chains and hydrophobic backbone, resulting in phase separation.<sup>[27]</sup> This morphological feature of PFSA ionomers is determining the formation of broad hydrophilic domains, which are delimited by the side chains of the polymer strand and constrained by the semi-crystalline domains of hydrophobic polytetrafluoro ethylene (PTFE) backbones.<sup>[28]</sup> The presence of solid-state organized domains constrains polymer swelling even when soaked in water by limiting the maximum hydration number. This feature reflects positively in the performance of a fuel cell since it limits the amount of free water that can possibly be in the membrane, avoiding the soaking of the whole cell under operation with high current densities. Additionally, the presence of broad hydrophilic domains results in low friction to the water transport.

# 2.2.2 sPPS:PBI-OO blends

sPPS is a relatively novel material for PEM application, having been introduced in 2007 by Schuster et al.<sup>[29]</sup>. The simple chemical structure of such polymer allows to achieve a maximum IEC of  $4.5 \, mmol \, g^{-1}$  with a sulfonation degree of 1, corresponding to 1 sulfonate group per phenyl ring. As can be observed from its monomer's structure, there is no possibility of spatial segregation between hydrophilic moieties from the less hydrophilic phenyl rings. On the contrary, a certain polarization is also present within phenyl rings due to the sulfone bridges. In addition, since also sulfonate functional groups are

directly connected to the poly-phenylene sulfone backbone and withdraw electronic charge fron the conjugated rings. This leads to a more homogenous morphology in which crystallization is far less present than in the other polymers and the leading interpretation consist effectively in a matrix of single polymeric strands immersed in water. As a result, sPPS can uptake much more water than Nafion<sup>™[14]</sup> due to the prevalence of ionomer-water interaction against ionomer cohesive forces. Therefore when employed on its own, this material is greatly affected by water activity of its surroundings. Indeed, when exposed to particularly dry environment sPPS becomes brittle and can easily fracture, while in moist conditions swelling and softening lead to concerning loss of mechanical performance and dimensional stability.<sup>[14]</sup> Lastly, when immersed in liquid water sPPS with a high sulfonation degree can be dissolved at high temperatures. Since a fuel cell operates in a wide range of relative humidities (or water activities), it is important to introduce mechanical stability in order to prevent embrittlement as well as inhibit the dissolution of the polyelectrolyte. One solution to both these problems is the blending of sPPS with polybenzimidazole (PBI) which possesses excellent film-forming properties and can act as a polymeric base through the imidazole ring which can develop an acid-base interaction with sulfonate groups in order to prevent dissolution through ionic crosslinking. However, acid-base interactions are characterized by a much less bonding energy than chemical crosslinking. This is the reason why at high temperatures and at high water activity the ionic bond may be lost. Since this blend has been developed for being a fluorine-free alternative to PFSA-based membranes, the reinforcement had to be realized with non-perfluorinated plastics. The material adopted for this thesis is a blend of 85 % sPPS-240 and 15 % PBI-OO with a reinforcement in porous PE characterized by a 50 % porosity.

# 2.3 CHEMICAL STABILITY

The cathode electrode constitutes a particular agressive environment for polymers due to the high electrochemical potential. Electrochemically, the cathode is concentrating the vast majority of electrocatalyst material and is often exposed to air, which even in absence of current flowing through the external circuit causes the potential to be high, defined as Open Circuit Voltage (OCV). Fuel cells are usually operated at temperaturse just below 100 °C to ease the removal of water through the cathode gas flow and at high relative humidity in

order to avoid membrane drying. However, such conditions lead to high water activity, which has been associated to the hydrolytic loss of sulfonate groups. Furthermore, it is possible to obtain formation of hydroxo- and peroxo- radicals at the cathode side in three main ways. Firstly, since membranes are thin polymeric materials, the hydrogen present at the anode can permeate through the membrane in a phenomena called hydrogen crossover. The quantification of this phenomena is expressed through an equivalent current and usually amounts to a few  $mA \ cm^{-2}$  of the membrane surface. Secondly, it is possible to obtain potentials approaching zero if the cathode flow is interrupted but the fuel cell continues to be operated galvanostatically. Such operation leads to the build up of hydrogen evolution reaction (HER), see Reaction 4, at the cathode and is usually used in a conditioning procedure called air starvation cycling. This operation aims at cleansing the platinum catalyst from sythesis byproducts before using the fuel cell exploiting abundant production of hydrogen, and radicals at the air cathode side.

$$2 H^+ + 2 e^- \longrightarrow H_2$$

$$\{4\}$$

Due to the importance of this procedure, more details will be provided in Subsection 3.4.1.

Alternatively, when the cell is operated at very low potential, the hydrogen peroxide formation reaction (see Reaction 5) becomes favoured by platinum electrocatalysts.

$$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$$
<sup>(5)</sup>

Since  $H_2O_2$  is not stable, it will decompose producing hydroxyl OH  $\cdot$  and peroxohydroxyl OOH  $\cdot$  radicals that can possibly bring harm to the polymer electrolyte. Additionally, peroxide formation is also possible at the anode side when the cell is kept at OCV conditions due to oxygen permeation through the membrane.<sup>[30]</sup> However, this last mechanism will be much less relevant in the study due to the testing protocols and materials adopted.

In particular, OCV conditions will be avoided and it is also relevant to consider two other factors:

- 1. Oxygen is less permeable than hydrogen;<sup>[31]</sup>
- 2. Degradation rate has been found to be proportional to platinum loading of the electrode in which it occurs. Since at the anode the loading is generally 1/8 of the cathode loading the rate of the reactions are expected to differ by roughly one order of magnitude;

For these reasons, this mechanism will be not discussed any further in this work.

# 2.3.1 PFSA

Degradation of PFSAs is mainly correlated to the loss of fluorine expressed by the Fluorine Emission Rate (FER). An accepted mechanism for degradation of the perfluorinated backbone considers the decomposition of peroxide into hydroxyl radicals which are able to attach the carboxylic acid ends of the polymer chain.<sup>[32]</sup> However, attack of side chain is considered to play a major role in PFSA degradation during fuel cell operation.<sup>[33]</sup> One of the proposed mechanisms consist in the attack by hydrogen peroxide of the sulfonic acid group, leading to the release of SO<sub>3</sub> and initiating the side-chain unzipping by leaving behind a terminal  $-CF_2 \cdot$  radical. This initiation eventually might propagate to unzip the side-chain until causing the cleavage of the perfluorinated backbone. Nevertheless, the engineering of scavenging additives has reached a level of maturity sufficient to enable deployment at industrial level of such compounds by increasing the lifetime of the membrane by a factor 10, compared to the pristine polymer.<sup>[34]</sup>

# 2.3.2 sPPS:PBI-OO blends

Being the material treated in this thesis a blend, it is necessary to discuss the chemical stability of both its components. For sPPS, the main focus has been pointed at its tolerance towards OCV conditions.<sup>[35]</sup> However, this resilience is boosted by the low permeability of the membranes to oxygen which halts  $H_2O_2$  formation at the anode. For a more realistic comparison of chemical stability between PFSA and sPPS it is necessary to consider the half-life of harmful radicals within them.<sup>[36]</sup> Hydroxyl radicals, OH  $\cdot$ , have an half-life in the range of microseconds within PFSAs due to the limited availability of reaction sites which effectively makes inorganic scavenging a viable solution. However, sulfonated polyphenylenes are subject to radical attack on the phenyl ring, which is the main constituent of the polymer and as a result the half-life of aggressive species is in the range of nanoseconds, too low to tailor a scavenging mechanism based on inorganic additives. As in PFSA, oxidative degradation may result in chain scission but additionally it may cause hydroxylation and

#### 2.3. CHEMICAL STABILITY

crosslinking. While hydroxylation drives the loss of IEC, oxidative crosslinking is the major cause of stiffening and embrittlement in hydrocarbon membranes. An important progress to the assessment of chemomechanical degradation in sulfonated polyphenylenes was obtained through humidity cycling tests. Since hydrocarbon polymers swell more than perfluorinated ionomers, membrane stiffening leads to a higher stress during humidity cycling. Ultimately leading to premature failure caused by fracturing or pinhole formation resulting in a loss of gas tightness by the membrane.

Regarding PBI-OO, it is known to be susceptible of facile oxidative degradation via midpoint chain scission and endpoint attack.<sup>[37]</sup> Being deputed to the film forming properties of the blend, its degratation might lead to the loss of this property and the provoke embrittlement of the membrane. It is also considered that the polymers used in this blend interact through an acid-base interaction which results in an ionical cross-linking trough an hydrogen bridge established between the sulfonate group of sPPS and the imidazolium ring of PBI-OO. Such interaction was found by Mack et al.<sup>[38]</sup> to greatly increase the chemical stability of PBI-OO but an excess of sPPS was correlated to an increase in chemical susceptibility, which is also the condition for the membranes adopted in this study.



In this chapter, processes, techniques and protocols are described to elucidate the background necessary for the following results and discussions. Since protocols are essentially a rearrangement of common procedures the constituent blocks are described in detail before introducing the overall testing. All procedures included in protocols which are correlated to a measurement are discussed in Section 3.3, while the peculiar conditioning, aging and recovery procedures are explained in Appendix B.

# **3.1** Processing methods

enThe processing methods described include the coating of catalyst and ionomer layers as well as the decal transfer of electrode materials onto Solid Polymer Electrolytess (SPEs) necessary to prepare Catalyst-Coated Membranes, CCMs.

# 3.1.1 Doctor blade coating

Doctor blade coating consists in the usage of a calibrated blade being slid over a substrate to disperse an ink with an homogenous thickness. In this work a Zehntner ZUA 2000.100 doctor blade was used, see Figure 3.1. This instrument has a width of 100 mm and the gap can be adjusted by rotating the two main crowns on its sides between 0 to 3000  $\mu$ m with 5  $\mu$ m steps. Blade's movement is executed by a TQC AB300 film applicator by means of a metallic bar which at

#### 3.1. PROCESSING METHODS

rest is positioned at the back end of the device, as shown on the left of Figure 3.1.



Figure 3.1: (*left*) TQC AB300 film applicator used to slide a blade over the substrate. (*right*) Zehntner ZUA 2000.100 adjustable doctor blade.

Before application, the blade is positioned over a substrate onto the film applicator, then around 5 mL of catalyst ink are positioned in front of the blade and then the applicator is activated. After application, the blade is cleaned and the wet layer is left to dry in the vent hood for at least one hour, unless specified differently. Followingly, coatings are cut into 7 cm x 7 cm squares and the platinum distribution is estimated by means of XRF spectroscopy, described in Section 3.2.1.

# **3.1.2** Decal transfer

The application of electrodes onto a membrane to prepare a CCM is done by calendering. The used calender was acquired from Saueressig Group of Matthews Europe GmbH and consists of two steel rollers with a chrome surface which can preheated at the desired temperature for improving adhesion among the assembly components. In this process, the gap between rollers is the parameter that can be set within an accuracy of 1  $\mu$ m, while the applied pressure is measured and expressed in *N/mm* since there is no way to measure the contact area of rollers and sample. An approximate method to estimate the average pressure applied on the sample is provided in Appendix A.

To proceed with lamination, an assembly must be prepared, which in the case of this work involves the stacking of 5 different layers. Two outer sheets of Am-

CHAPTER 3. METHODS



Figure 3.2: (a) Example of an assembly ready to be calendered, the upper wrapping foil was removed to expose electrodes sandwiching the membrane. (b) Scheme of the calender used for transferring catalyst layers onto membranes.

meflon® are used to wrap the membrane sandwiched between catalyst layers cut-outs coated as well on Ammerflon®. In Figure 3.2a, it can be seen the membrane sandwiched between electrodes while it is laying on the lower wrapping foil. As can be seen in Fig. 3.2b, the sample is introduced in the calender to pass through the rolls and be collected on a lower plate following the path described by the green arrow. After lamination, Ammerflon® foils which were previously carrying the catalyst layers are peeled away and a CCM is then ready for testing, see Fig.3.3 for visual reference.

# **3.2** Ex situ evaluation methods

The ensemble of experimental techniques adopted in this study is conceived in order to quantify the load of electrocatalyst in the catalyst coatings, track the evolution of electrochemical behavior in-situ as well as in-operando and to assess the chemical and physical features of the sample after testing. The minimum background for the upcoming discussions is provided in this section.

#### 3.2. EX SITU EVALUATION METHODS



Figure 3.3: (a) CCM obtained by decal transfer of the calendered assembly. (b) Ammerflon® substrates that were coated with catalyst layers after peeling off. It is possible to see some black small residuals along the edges of each substrate.

# 3.2.1 XRF Spectroscopy

X-Ray Fluorescence consists in the measurement of X-ray secondary emission from a sample excited with a high energy gamma or X-ray beam. In this technique, an impinging X-Ray beam is responsible for the ionization of a target atom by releasing electrons even from inner shells. Secondary emission takes place when the vacant position is replaced by the relaxation of an electron placed in a neighbouring shell with subsequent release of the energy difference in the form of a photon. The secondary emission energies are specific and therefore energy dispersive analysis can be used to perform quantitative chemical identification. This technique is particularly convenient for the estimation of platinum content in catalyst layers for PEMFCs due to the high cross-section of heavy elements towards this process. In particular, through the comparison with a reference material it is possible to estimate the *platinum loading*, which corresponds to the area distribution of Pt and is usually expressed in  $mg_{Pt} cm^{-2}$ . For this thesis, the scope of such characterization is therefore limited to quantify the amount of platinum present in the prepared electrodes. To do so, a Fischerscope® X-Ray XDV from Helmut Fischer GmbH has been used.

# 3.2.2 ATR-FTIR

Attenuated Total Reflectance-Fourier Transform Infrared consists in a spectroscopic technique aiming at the identification of chemical bonds within a material. This is made possible by the use of infrared photons, which carry energies compatible with excitation of molecular vibrational modes. Even though said vibrational modes consist in the concertated movement of all the atoms composing a molecule, the amplitude of such vibrations is not evenly distributed and can be often considered as localized in a specific bond. It has also to be said that the bonds between two atoms can be considered as a harmonic oscillator, whose vibration frequency depends on its strength. While the nature of atoms participating in said bonds plays a great role in determining oscillator's characteristic frequency, influence due to further atoms being part of the same molecule can be described as a secondary effect. Hence, the possibility for infrared spectroscopies to diagnose presence of chemical bonds within a sample. Fourier Transform Infrared (FTIR) spectroscopy employs an infrared source with a broad spectral emission which is directed to a Michelson interferometer and subsequently to the sample and a detector. By displacing the moving mirror within the interferometer, it is possible to modify the spectral composition of the probing radiation in accordance to the shift in interference conditions. Then, the sample is exposed to the mentioned probing radiation and the trasmitted component is collected and quantified through a detector. By measuring the overall incident radiation at different displacements of the moving mirror, an interferogram is collected. Afterwards, the dependency of measured beam intensity on displacement can be converted by means of Fourier Transform into the spectral composition. For measurements reported in this work, an ALPHA II from Bruker Corporation with an Eco-ATR module has been used. Instrumentation used within this work was set in Attenuated Total Reflectance (ATR) configuration, therefore the beam is directed into a ZnSe crystal over which the membrane samples are pressed to obtain a clean contact. In this setup, the beam propagates within the crystal due to the phenomena of total reflectance. However, attenuation might occur in relation to the fact that at the interface between crystal and sample an evanescent wave is formed and propagates outside the crystal with an expontentially-decaying intensity. In turn, if the sample presents characteristic absoprtion for at least one of the incoming wavelengths, transmission through the crystal will not be ideal and dimming in the transmitted signal

#### 3.3. IN-SITU EVALUATION METHODS

will be recorded. Since in this configuration radiation doesn't cross the sample, all the spectras will be reported in terms of normalized absorbance over the tallest absorption peak.

# 3.2.3 SEM

Scanning Electron Microscopy is based on a focused electron beam being scanned over the surface of a sample. Two instruments have been used to obtain the images reported within this work.

To measure the thicknesses of employed layers, polihed sections were prepared and analyzed with a Supra 55VP from Carl Zeiss AG, where an electron beam is produced by thermal field effect and is subsequently focused by a series of electromagnetic lenses (*coils*). Imaging is possible in this instrument through Angular-selective Backscattered-electrons (AsB) and Secondary electrons (SE2) detectors. An AsB detector allows to obtain a certain degree elemental contrast due to higher cross section for electron backscattering for heavier elements. Meanwhile, the SE2 detector is mainly employed to achieve better topological resolution as a result of the lower emission depth associated with this type of radiation. However, the main goal of this technique to obtain micrographs of a sample's surface to investigate its topology and nano/micro-structures.

Additionally, in order to obtain highly magnified micrographs of every layer, a Merlin® FE-SEM from Carl Zeiss AG was used. In this instrument, electron emission takes place due to field effect, allowing for narrower probing beams than as seen for the previous SEM and leading to smaller aberrations. The electron gun is used in combination with an *InLens* detector which can collect either secondary or backscattered electrons. Main advantage of this detector consists in the placement directly within the electromagnetic lenses, allowing to virtually eliminate any aberration.

# 3.3 *In-situ* evaluation methods

Electrochemical experimental techniques were used to characterize the prepared CCMs in terms of performance and relevant properties. In order to obtain realistic estimates of the performance, a  $25 cm^2$  serpentine flow field was employed, while to obtain reliable estimates of the physico-electrochemical features, a differential flow field was preferred. These two setups differ in the length of the gas transport trenches. In a serpentine flow field the gas flows over a GDL for about  $40 - 45 \, cm$  inducing thermal, pressure and humidification gradients, as it would occur in a full-size PEMFC stack for automotive applications. On the contrary, the differential operation of a fuel cell implies the adoption of much shorter gas flow paths (about 4 cm), which take place in trenches designed to minimize pressure gradients. In all cases, the fuel cells were tested on a HORIBA FuelCon Evaluator C10-LT test station.

# 3.3.1 POLARIZATION CURVES

The performance of a fuel cell is defined by the dependence of output load on the current density flowing through the device. Measuring these quantities at different current densities results in a characteristic curve, called polarization or I-V curve. Polarization curves are tipically collected galvanostatically because the current in a fuel cell affects its chemical and thermal equilibrium, while the voltage generated at the electrodes can be dissipated with little or no influence on the device. Therefore, after setting the operating conditions according to Table 3.1, a current is established and held for a defined *holding time*.

	Standard	Cold & Wet	Hot & Dry	$O_2$
<b>T</b> [° <i>C</i> ]	80	40	85	(80)
<b>RH</b> [%]	90 (100)	95	30 (0)	(100)
<b>p</b> an <b>/p</b> cat [bar]	2.2/2 (2.0/2.0)	1.5/1.3 (2/2)	2.2/2 (2/2)	(2.2)
$\lambda_{an}/\lambda_{cat}$	1.5/1.8 (-/-)	1.5/1.8 (-/-)	1.5/1.8 (-/-)	(-/-)
Qan/Qcat [Nl/min]	(2/5)	(2/5)	(2/5)	(2/5)

Table 3.1: Parameters for the collection of polarization curves from a serpentine setup in significative conditions. Differential setup parameters are reported in round brackets when different from serpentine setup ones. For differential setup, stoichiometry is not fixed, but rather is flow, *Q*.

The voltage is measured as the average over 30 seconds. Since two different sets of parameters have been adopted depending on the setups used, this distinction is also shown in the tables by placing the values relating to the differential setup between round brackets.

From this measurement, it is possible to obtain an average value and its standard deviation, which will be used for the error bars reported in the results. Current setpoints and corresponding holding times are summarized in Table 3.2.

Polarization curves can be elaborated into the so-called Tafel plot, which is

#### 3.3. IN-SITU EVALUATION METHODS

j [A cm <sup>−2</sup> ]	(4)	(3.5)	3	2.5	2	1.5	1	0.5	0.3	0.2	0.1	0.05	0.025	0.01	0
<b>t</b> [min.]	(10)	(10)	10	10	10	8	6	4	4	4	4	4	2	1	1

Table 3.2: Current density steps and holding times for the collection of polarization curves within a serpetine setup. Differential setup parameters are reported in round brackets when different from serpentine setup ones.

functional to focus attention on the low current density regime since it represents the logarithm of the current density on the *x*-axis. To display the Tafel plot, some processing of the original data is required. Indeed, the measured potential is corrected for the ohmic resistance obtained from HFR measurements described in 3.3.2 and the current density is normalized for the ECSA which is obtained through cyclic voltammetry (see Section 3.3.3). Then, *y*-axis reports the overpotential  $\eta$  from OCV, instead of the potential measured during the polarization curve. Such overpotential is obtained by the formula:

$$\eta(j_{ECSA}) = U_{OCV} - U(j_{ECSA}^{iR-free})$$
(3.1)

# 3.3.2 IN-OPERANDO EIS

EIS is a powerful tool for the evaluation of complex electrochemical devices since it allows to describe the behavior by fitting an Equivalent Circuit Model (ECM), where each element can be assigned to a single mechanism. Also, this technique can be executed *in operando*. This technique requires to stimulate an electrochemical cell with an electrical sinusoidal signal at various frequencies and to measure the response. In this work, all EISs has been performed galvanostatically, meaning that the input signal corresponds to an Alternating Current (AC) current, which induces a periodic response in the potential. Since a signal is described by an amplitude and a phase, the response is also analyzed in terms of these quantities which are embedded into a complex property called impedance,  $Z(\omega)$ . The definition of impedance is:

$$Z(\omega) = \frac{V_{AC}(\omega, t)}{i_{AC}(\omega, t)}$$
(3.2)

Where  $Z(\omega)$  is the impedance at a specific frequency,  $V_{AC}(t, \omega)$  is the periodic component of the potential measured at the electrodes while  $i_{AC}(t, \omega)$  is the AC input. Experimentally, impedance magnitude ( $Z_0$ ) and phase shift ( $\Phi$ ) are measured for the response signal. Subsequently, these two measures are combined

to factor impedance into its real (Z') and imaginary (Z'') components.

$$Z(\omega) = Z'(\omega) + Z''(\omega) = Z_0(\omega)cos(\Phi(\omega)) + jZ_0(\omega)sin(\Phi(\omega))$$
(3.3)

Measured impedance and phase are usually reported in two different plots, the Nyquist plot and the Bode plot, an example of which is shown in Figure 3.4. A Nyquist plot consists of a Gauss plane plot of the impedance with a reversed complex axis due to the fact that any electrochemical behavior is expected to cause a phase shift in between an ideal resistor ( $\Phi = 0^{\circ}$ ) and an ideal capacitor ( $\Phi = 90^{\circ}$ ). Therefore, it is more convenient to represent measured quantities in the first quadrant. A Bode plot consist of the spectral representation of impedance magnitude and phase shift.

A common equivalent circuit used to describe PEMFC spectra, is schematized in



Figure 3.4: Example of (*left*) Nyquist plot and (*right*) Bode plot obtained from measuring EIS at a fixed current density of 0.5  $A cm^{-1}$ . The sample was being tested in CW conditions.

Figure 3.5a. Such ECM considers three main mechanisms taking place within the fuel cell. First, an ohmic resistance is related to the ionic electrical current flowing through the proton-exchange membrane. This quantity is reported as High-Frequency Resistance (HFR) Then, it is assumed that the major contributions to the electrochemical behavior of a cell are the reactions occurring at the electrodes, which represent faradaic processes. This type of mechanisms are modeled in EIS as a resistor in parallel with a unideal capacitor, also called an R-CPE element.

#### 3.3. IN-SITU EVALUATION METHODS

Non-ideality of a capacitive behavior is often embodied by a Constant Phase Element, whose description can be semplified as a leaking capacitor that cannot retain a phase shift of the input signal of exactly 90°.



Figure 3.5: Equivalent circuits used to model the observed EIS behavior of a PEMFC. Drawn using Web Editor from Circuit Diagram.

To each element of the equivalent circuit it is possible to attribute a specific feature in the collected spectra. Since ionic resistance is represented as a resistor in series to all the other elements of the circuit, it will coincide with the intercept between measured EIS and Z' axis at high frequency. Since anodic reaction kinetics are supposed to be faster than its cathodic counterpart, the corresponding semicircle should be placed at higher frequencies. Therefore, the semicircular features are assigned to anode and cathode from left to right of the Nyquist plot, respectively. Since the impedance is normalized by the area of the sample, measured parameters are expressed in terms of Area-Specific Resistance (ASR) and their value is reported in  $m\Omega cm^{-2}$ . Throughout this study, the anodic reaction resistance is called  $ASR_{an}$ , while the resistive element is associated to  $ASR_{LFR}$  where Low-Frequency Radius (LFR) stands for Low-Frequency Radius. Contributions to  $ASR_{LFR}$  are the mass transport resistance,  $ASR_{mt,cat}$ , and cathodic reaction,  $ASR_{ct,cat}$ . In case anodic kinetics are sufficiently fast and require low activation overpotential, an alternative feature might appear right after intercept with the real axis. Such feature is a linear slope which can be modeled through a non ideal capacitance Trasmission Line Model (TLMQ). This peculiar circuit element allow to account for the distribution of path lengths within a porous media such as the catalyst layer for protonic conduction, called followingly  $ASR_p$  standing for protonic resistance. This circuit element has been described in detail by Landesfeind et al.<sup>[39]</sup>, for the reader's reference.

# **3.3.3** Cathode Cyclic Voltammetry

CV is an important electrochemical technique, especially when it comes to characterize Pt/C electrocatalyst materials. The setup used for in-situ CV is schematized in Fig.1.2. Considering that the electrode limiting the performance of a PEMFC is the cathode, this setup considers the  $H_2$  electrode to act as counter electrode (CE) and reference electrode (RE) due to very high kinetics of the hydrogen oxidation reaction (HOR) (Reaction 2). An  $H_2/N_2$  atmosphere is estabished at anode and cathode layers, respectively. The anode flow is set to  $Q_{an} = 0.2 Nl/min$  flow at the anode while cathode valve is closed. The cell is kept at 80 °C with a Relative Humidity (RH) of 100%. Complementarily, the electrode in  $N_2$  acts as working electrode (WE) and is the material under investigation. A triangular potential is applied at the WE, sweeping between 0.9 V and 0.07 V Vs RHE at a scan rate v = 50 mV/s and the current is recorded. For each measurement, 5 cycles are performed and the last 3 are averaged together to obtain a more reliable representation. Except where otherwise specified, only these averaged curves are shown. Given the composition of a catalyst layer, the expected signals are all related to the Pt nanoparticles and to the double step Hydrogen Underpotential Deposition ( $H_{UPD}$ ), or desorption depending on the scan direction, as reported in Figure 3.6.



Figure 3.6: Example of CV obtainable from a PEMFC cathode.

This voltammetric technique is adopted to estimate the Electrochemical Surface Area and hydrogen crossover current associated with the electrochemical reduction of H<sub>2</sub> permeating through the membrane. Estimation of ECSA is possible from the measurement of charge associated with the desorption peaks of  $H_{UPD}$ , through Eq. 3.4.

$$ECSA = \frac{A_{H_{UPD},des}}{\nu \,\mu_{Pt}} \tag{3.4}$$

Where  $A_{H_{UPD},des}$  is the area of  $H_{UPD}$  desorption peaks as shown in the previous figure as the light blue area, v is the scan rate of the potential sweep and  $\mu_{Pt} = 210 \ \mu C \ cm^2$  is the area-specific charge associated with the formation of an hydride monolayer on Pt. For the estimation of H<sub>2</sub> crossover current estimation, the double layer region of a CV is considered.<sup>[40]</sup> In this region, there are only two contributions to the measured current, firstly a Double Layer Current (DLC) associated with the dielectric charge and discharge of the metalelectrolyte interphase which follows a purely capacitive behavior, meaning that DLC in the positive (anodic) and negative (cathodic) scan have identical but opposite intensities. Due to the potential window at which DLC is observable (between 0.4 V and 0.5 V), H<sub>2</sub> reduction at the WE is expected to possess a sufficiently high overpotential to be substantially limited by mass transport. For this reason, the current contribution incoming from this process is assumed to be contant within the double layer region. Therefore, H<sub>2</sub> crossover current can be estimated as the average of anodic and cathodic sweeps currents within the DLC regions.

# 3.3.4 LIMITING CURRENT

Limiting Current methods are exploited to estimate the oxygen transport resistance ( $R_T$ ) across GDLs, MPLs and catalyst layer.<sup>[41]</sup> Oxygen transfer resistance is defined as the change in oxygen concentration between flow-field and the cathode electrode catalyst divided by the normal molar flux of oxygen  $N_O = i/4F$ . Since in limiting current conditions the concentration of O<sub>2</sub> at the electrode is negligible,  $\Delta c_{O_2} = c_O = p\chi_{O_2}/RT$ . Therefore gas transport resistance can be explicitated as in Eqn. 3.5

$$R_T = \frac{4F\chi_{O_2}^{wet}p}{i_{lim}RT}$$
(3.5)

Where  $R_T$  is the oxygen transport resistance, F is the Faraday's constant,  $\chi_{O_2}^{wet}$  is the molar fraction of oxygen in the wet gas flow, p is the pressure within the cell,  $i_{lim}$  is the limiting current, R is the universal constant of gases and T is tem-

perature. Since this method is heavily reliant on the homogeneity of conditions over the sample, it can only be performed in differential cells, which possess a much shorter and straight flow field (each trench is 4 cm long), in combination with very high stoichiometry flows. To measure the value of limiting current, it must be accounted that below 0.2V Pt electrocatalysts undergo parasite reactions that arise by further decreasing the potential. Firstly, they promote a 2 electrons oxygen reduction to hydrogen peroxide, leading to a decrease in overall current. Followingly, the activation of HER at the cathode can occur as the potential approaches 0V, resulting in a sudden increase in current density due to the rapid kinetics of such reaction. Accounting for these additional details, the correct assignment of limiting current is the one reported in Figure 3.7a. To halt oxygen transport, different mechanisms can take place but all of them can be distinguished by their dependence on pressure (Eqn. 3.6).

$$R_T = pR_P + R_{NP} \tag{3.6}$$

Among the pressure-dependent mechanisms agglomerated in  $ASR_p$ , it is possible to mention the intermolecular diffusion which dominate the transport properties of large pores of the GDL. Pressure-independent contributions to  $R_{NP}$  can be attributed to Knudsen diffusion in smaller pores and to gas diffusion through ionomer and wet layers covering the electrocatalyst. Knudsen diffusion defines the stochastic displacement of gas molecules within pores possessing diameter smaller than the mean free path of gaseous species.

These two types of contributions are distinguished by measuring  $i_{lim}$  at different pressures with fixed  $\chi_{O_2}^{wet}$ . The molar fraction of oxygen in the wet flow is first adjusted to 1 % and then to 4 %. In Fig. 3.7a, the complete measurement is reported. Then,  $i_{lim}$  is extracted as previously described. The obtained values are then used to calculate  $R_T$  which dependency on pressure is depicted in Fig. 3.7b and through a linear regression is possible to extract  $R_{NP}$  as the intercept and  $ASR_p$  as the increase of  $R_T$ . Since no explicit dependency is expected from  $\chi_O$ , repetition of the mentioned analysis with different values for this parameter enables independent estimation of oxygen transport resistance. By applying two distinct set of conditions to the sample, it is possible to evaluate the correlation between oxygen transport resistance and presence of liquid water. Firstly, limiting current is studied at 80 °C and 80 % *RH* to represent a condition of sufficient humidification but free of liquid water. Secondly, the experiment has been re-

#### 3.4. TEST BENCH OPERATION PROTOCOLS



Figure 3.7: (a) Current density measured at different potentials with an O<sub>2</sub> molar fraction of  $\chi_{O_2} = 0.01$  at 80 °C and 80 % RH. (b) Linear regression to extrapolate the pressure-dependent and independent contributions to oxygen transport resistance.

peated at 40 °C and 100 % *RH*, which should ensure the presence of liquid water, possibly soaking of electrodes and GDLs. In both testing conditions the total gas flows are set at  $Q_{an} = 2Nl/min$  and  $Q_{cat} = 5Nl/min$  and the O<sub>2</sub> individual flow is adjusted to obtain the desired molar fraction at the different testing conditions by accounting for the difference in water vapour pressure at 40 °C and 80 °C.

# **3.4** Test bench operation protocols

Different protocols were adopted for electrochemical testing of the samples to better identify the factors influencing performance stability. Due to the relevance of this work, the conditioning procedure is described in this chapter before detailing automated test protocols. Meanwhile, for all other procedures further details are placed in Appendix B.

# 3.4.1 CONDITIONING PROCEDURE

Conditioning, also referred as *Break-in*, is meant to be a procedure that allows freshly assembled PEMFCs to reach maximum power density.<sup>[20]</sup> A particular phenomena taking place during this procedure consists in the cleaning of Pt nanoparticles from organic residuals. Since it takes place at the first utilization of the device it plays a crucial role in the pathway taken by degradation of its components. Therefore, harmonized procedures have been established by DOE and European Union (EU) to enable comparability of studies in this



sector. The procedure adopted in this work consists of cathode starvation cycles interspersed by potentiotatic holds at low potential, as plotted in Fig. 3.8a. This

Figure 3.8: (a) Overview on the mixed potentiostatic and galvanostatic control during cathode starvation conditioning and (b) overlapped cycles with progressive increase of opacitiy (early cycles are more transparend, late cycles more opaque).

steps begins with the equilibration of conditions at 80 °C with 95 % RH and an outlet pressure of 1.5 bar with H<sub>2</sub>/Air respectively at the anode and cathode. Flows are set at costant  $\lambda$ , for the cathode  $\lambda_{cat} = 4$  while for the anode  $\lambda_{an} = 3$ . Potentiostatic holds are done at 0.35 V for 5 minutes at the beginning, once half the cathode starvation cycles have been performed and at the end of this procedure. Each cathode starvation cycle (see Fig. 3.8b) consists in a galvanostatic hold at  $1.3 A cm^{-2}$  for 60 s after which air flow at the cathode is interrupted for 45 s and the current is contestually decreased to  $0.5 A cm^{-2}$ . During cathode air flow interruption, the potential initially soars due to the reduced current density, but soon it starts to decrease as a result of residual oxygen consumption at the cathode side. Once O<sub>2</sub> concentration becomes negligible, potential drops causing the control to switch into potentiostatic mode at 0 V until the cycle ends. If the potential during galvanostatic hold at  $1.3 A cm^{-2}$  decreases below 0.35 V, current density is reduced in  $0.1 A cm^{-2}$  steps until potential increases over this threshold. The number of cycles varies from 120 for the benchmarking and differential cell protocols to 20 for the process optimization and conditioning protocols.

#### 3.4. TEST BENCH OPERATION PROTOCOLS

# **3.4.2** Benchmarking protocol

A benchmarking protocol consists in a sequence of procedures which are designed to extract performance of samples in realistic operative conditions and quantify the tolerance to harmful operation. An outlook to the protocol is reported in Figure 3.9. To obtain reliable information about the performance of samples, polarization curves (see Section 3.3.1) are collected at different temperatures and relative humidities after an initial conditioning (3.4.1) but also at EoT. Before the characterization of performance, an initial evaluation of the catalyst is assessed by means of CV. The first accelerated stress test procedure enables to characterize the tolerance to Pt dissolution (B.1.1). Afterwards, AST2 is performed to establish the tolerance of fuel cells to carbon corrosion conditions (Appendix B.1.2).



Figure 3.9: Schematic representation of the steps performed in the benchmarking protocol.

#### **3.4.3** Process optimization protocol

Since the previous protocol proved to be unviable for some of the samples prepared in this work, a procedure with shorter conditioning and no Accelerated Stress Tests (ASTs) was prepared. The goals of this procedure were firstly to track performance decay across conditioning for samples prepared through different routes (discussed in Section 4.2.2), to verify catalyst activation and crossover current through CV. It was decided to repeat twice the measurement of I-V curves to evidence whether operation also contributed to repentine performance loss.



Figure 3.10: Schematic representation of the steps performed in the process optimization protocol.

3.4.4 Conditioning protocol

This protocol was developed as a modification of the previous one in order to investigate with more focus on the effect of conditioning cycles over the performance of prepared fuel cells. Therefore, the two sets of I-V curves and CVs were split before and after the shortened conditioning. Furthermore, Galvanostatic EIS was collected before, during and after the step of interest. EIS was collected from 100 *kHz* to 1 *Hz*, with 20 points per decade, an amplitude of 3 *mV* for the AC signal at a current density of 10 *mA cm*<sup>2</sup> with  $\lambda_{an} = 3$ ,  $\lambda_{cat} = 4$  at 80 °C and 95 % *RH*.



Figure 3.11: Schematic representation of the steps performed in the conditioning protocol.

# 3.4.5 DIFFERENTIAL CELL CONDITIONING PROTOCOL

A differential cell setup was adopted to estimate more reliably properties of CCMs, including limiting current measurements and accessibility to I-V curves with pure oxygen flow at the cathode. After measurements in *Hot & Dry* conditions, a sulfonate dissolution procedure needs to be performed. Such dissolution

# 3.4. TEST BENCH OPERATION PROTOCOLS

procedure is necessary since it is known that at reduced hydration sulfonate groups tend to adsorb on Pt surface, causing poisoning and ECSA losses. A detailed description of this procedure is reported in Appendix B.1.



Figure 3.12: Schematic representation of the steps performed in the differential cell conditioning protocol.



In this section, the materials and the experimental approaches used in the development of this work are detailed.



# 4.1.1 Electrodes

Catalyst layers used for the assembly of CCMs were prepared in-house by using a carbon-supported platinum electrocatalyst (Pt/C) and Nafion<sup>TM</sup> D2020 ionomer with an EW of 1100 *g/mol*. The electrocatalyst adopted for the cathodes is TEC10E50E provided by Tanaka Holdings Co., Ltd. characterized by a 50 % *m/m* content of Pt nanoparticles. The ionomer dispersion is added to the catalyst powder together with additional solvents to prepare an ink that subsequently is bead-milled to finally be coated by doctor-blading on fiber glass-reinforced PTFE foils supplied by Ammerflon®. A similar procedure was followed to prepared anode catalyst layers but the adopted electrocatalyst is Elyst Pt20 0390 provided by Umicore Fuel Cell & Stationary Catalysts. The loading of electrodes used in this study is  $0.4 \pm 0.04 mg cm^{-2}$  for cathodes and  $0.05 \pm 0.01 mg cm^{-2}$  for anodes.

### 4.2. OUTLINE

# 4.1.2 Thin Nation<sup>TM</sup> D2020 layers

Thin ionomer layers were prepared out of a Nafion<sup>TM</sup> D2020 dispersion in order to be used as intermediate layer, or IL, between electrodes and membranes. The thickness of such layers is around 1-2  $\mu$ m obtained by doctor blade coating on Ammerflon® or ETFE foils.

# 4.1.3 Membranes

The PFSA membrane used in this work is supplied by W. L. Gore & Associates, Inc., mode M765.08 with a thickness of 8  $\mu$ m, presents an ePTFE reinforcement and is engineered with additives to contrast chemical degradation of the ionomer. Membranes are also provided as part of the public project Beyond-PFSA funded by BMBF in joint development with Fumatech BWT GmbH as well as the institutes Centre for Solar Energy and Hydrogen Research Baden-Württemberg (ZSW), Max-Planck-Institute for Solid State Research and Agricultural University of Georgia. These membrane consist in a blend with 85 % sPPS-240 and 15 % of PBI-OO with a porous PE reinforcement with an overall IEC of 2.4 *mmol/g*. The used PE has a 50 % degree of porosity The membranes were originally 10  $\mu$ m thick, 5 of which being the reinforcement layer. However, during a standardisation procedure performed at Max-Planck-Institute, membranes were pulled in a A4 frame, causing thickness to shrink to 5-8  $\mu$ m in the central part of the sheet.

# 4.2 Outline

Experimental targets evolved during the thesis work in order to pursue two main targets of the joint project: performance improvement and progressive elimination of perfluorinated materials.

# **4.2.1** Performance improvement by interlayer thickness reduction

The initial step involved further development of the process studied by a forecoming student involving sPPS:PBI-OO membranes. The most effective process developed by my predecessor involved the addition of a Nafion<sup>™</sup> layer

on top of catalyst layers before lamination with the membrane to constitute a binding interlayer with a thickness of around 2  $\mu m$ . The introduction of an additional layer was functional to the successful preparation of CCM and was performed by coating a thin layer of Nafion<sup>TM</sup> on Ammerflon® foil which was then transferred onto the catalyst layer through decal transfer. However, Ammerflon® foils have a patterned surface due to the intertwined glass fibers, which was noted to be retained by the interlayer at its surface. Furthermore, this uneven substrate poses a lower limit for the thickness achievable by doctor blading. In order to lower the wet layer coating thickness from 20  $\mu m$  to 10  $\mu m$ , an unpatterned ETFE foil was chosen as an alternative to Ammerflon®. A sample obtained through this modified route was compared to the best sample prepared until then though a benchmarking protocol as detailed in Section 5.1.

# 4.2.2 Decal transfer without Nation<sup>TM</sup> Interlayer

While handling of sPPS:PBI-OO membranes, it was noticed that the srface pattern of Ammerflon® could be transferred if a wet sample was left to dry on it, as reported in Fig 4.1a. This phenomena could only be explained by softening of the material associated with high degree of hydration. Furthermore, during the final stages of drying, a certain degree of adhesion was manifested by the tendency of Ammerflon® foil to be bent by the shrinking membrane (Fig. 4.1b). Since the core target of the research project is to study performance of



Figure 4.1: (a) First observation of softening in wet conditions of sPPS:PBI-OO membranes. (b) Tangential strain evidencing adhesion between Ammeflon foil and membrane.

sPPS:PBI-OO membranes, finding processing windows that would allow the removal of Nafion<sup>™</sup> interlayers is of major interest, also in the perspective of

## 4.2. OUTLINE

assessing the compatibility of such membranes with state-of-the-art PEMFC electrodes. As a consequence, decal transfer was attempted at different states of drying for the membrane. In order to have more control over the humidifaction state of the membrane during lamination, the assembly was not preheated and the calendering rolls were kept at the minimum operation temperature of 40 °C. At first, smaller CCMs were prepared in order to allow a higher number of trials with the available material. It was noticed that a certain freedom in the amount of wetting was enabled by higher compression during lamination, as can be seen in Fig. 4.2b it was possible to achieve successful transfer by laminating the assembly with membranes still featuring a minimal amount of liquid water on its surface denoted by wetting of the catalyst layer underneath the membrane in Fig. 4.2a. However, when dealing with bigger samples, a drier membrane was



Figure 4.2: (a) Picture of the membrane to highlight membrane wet state during assembly (b)Successful decal transfer of catalyst layers onto sPPS:PBI-OO membrane through calendering at 40 °C with 100  $\mu$ m compression, causing a line pressure of 200 *N*/*mm*.

needed since wet layers would eventually be squeezed into localized spots of the sample leading to no transfer, as reported in Fig. 4.3a. Since it was also difficult to obtain homogeneous drying just by leaving the membrane on Ammerflon® foil, a frame was designed and 3D-printed (see Fig. 4.3b). The usage of a 3D printed frame allowed also to flatten the membrane before lamination as it would be provided with some wrinkles and after soaking it would appear like in Figure 4.4. A processing route for the preparation of CCMs employing sPPS:PBI-OO

### CHAPTER 4. EXPERIMENTAL



Figure 4.3: (a) CCM flattened on a vacuum plate with an untransferred spot which was found to be soaked after calendering, possibly due to water displacement during compression. (b) 3D-printed frame for homogeneous drying with a mounted membrane ready for assembling.

membranes featuring only easily upscalable steps was therefore established.

As a result, the process optimized with respect to the performance accessible after conditioning by sparsely investigating the role of calendering temperature and the presence of residual solvent, ethylene glycol (EG in the graphs), to act as a plasticizer within the catalyst layer. Results are discussed in Section 5.2.

# 4.2.3 Effect of Nafion<sup>™</sup> interlayer on performance and durability of CCMs

The effect of adding a Nafion<sup>™</sup> between catalyst layers and membranes was investigated by using the Conditioning protocol (Section 3.4.4). Firstly, the effect of such additional layer was addressed with respect to CCMs based on Gore SELECT M765.08 membranes and discussed in Section 5.3. Followingly, the same has been done for CCMs based off sPPS:PBI-OO membranes, with the only peculiarity that a sample has been prepared with interlayer solely at the cathode side to verify if the performance loss could be attibuted to the activity of a single electrode. This aspects are reported in Section 5.4. After in situ testing, also ex situ techniques were applied to verify the state of studied samples, such as ATR-FTIR and SEM.

### 4.2. OUTLINE



Figure 4.4: Soaked sPPS:PBI-OO membrane just framed to start the drying necessary to achieve the desired moistening degree.

# **4.2.4** Differential cell study of Nafion<sup>TM</sup> interlayer influence on interfacial stabilization

Once performance degradation associated to the interface electrode-sPPS:PBI-OO had been assessed, a more reliable experimental setup was implemented to provide estimations of electrochemical and physical descriptors generally adopted by the sectorial scientific community. This setup is characterized by the use of a differential setup which includes a modified flow field and testing parameters, with the intent of providing more even and controlled conditions over the whole active area. The flow field for differential setup is consisiting of a graphite trenched slab similarly to the one shown in Figure 1.3a. However, in this case with straight trenches and an active area of  $4 \ cm \times 3 \ cm$ . Additionally, mass flows set for tests in this setup are generally higher, as described for each technique individually in Chapter 3. This setup allows to reliably perform galvanostatic EIS at every current density set during measurement of polarization curves. Furthermore, limiting current measurements are also made possible by the high flows and low pressure drop achievable by the modified flow field.



# 5.1 Performance improvement by interlayer thickness reduction

Performance obtained from samples in which the Nafion<sup>™</sup> IL was prepared on Ammerflon® or ETFE foil is compared for all measurements in Fig.5.1. The two samples differ because of the thickness set on the adjustable blade for coating the Nafion<sup>™</sup> dispersion onto the substrates. On Ammerflon<sup>®</sup>, the gap was adjusted to 20  $\mu m$  while on ETFE the same was set to 10  $\mu m$ . Since the employed Nafion<sup>TM</sup> D2020 dispersion has a concentration of 20 % m/m and density of the dry layer is expected to be around 2  $g cm^{-3}$ , thickness of the obtained ionomer layer is supported to be around 1/10 of the gap. It can be immediately noticed that two groups can be distinguished for both samples with respect to performance output. The first, is consisting of polarization curves with a maximum current density above  $1.5 A cm^{-2}$  and includes only measurements before AST2. Secondly, a group of polarization curves exhibiting low performance is recorded after carbon corrosion protocol. This distinction is symptomatic of an abrupt loss of performance. A possible explanation resides in the fact that PFSA membranes normally feature inorganic additives to scavenge the hydroxyl radicals that may form when the potential becomes high enough to trigger water electrolysis, as in AST2 since the potential is swept between 1 V and 1.5 V.

Nevertheless, the proposed process based on ETFE carrier film and thinner



Figure 5.1: All the measured polarization curves from the benchmarking protocol for CCMs prepared with sPPS:PBI-OO membranes and with interlayers originally coated on (a) Ammerflon® with 20  $\mu m$  gap and (b) ETFE foils with 10  $\mu m$  gap.

interlayer allows the achievement of higher current densities especially for I-V curves collected until AST1 as well as a more even performance at the various conditions tested at BoL. This is shown in Fig. 5.2 by comparison of the maximum power output achieved during each polarization curve measurement. In



Figure 5.2: Comparison of the maximum power density output at different steps of testing between CCMs using an interlayer prepared with 20  $\mu m$  gap on Ammerflon® (*light blue*) or 10  $\mu m$  gap on ETFE (*light green*). Percentual increase in performance is shown through a the green line.

addition, it is noted that this modified procedure leads also to an improved performance retention across AST1, which simulates 30 thousands load varia-

tions on the sample since performance improvement moves up from 25% to 50%.

Furthermore, it is noted that performance improvement is substantially lost after AST2 which is also reflected by the ionic resistance measured for both samples before and after test. In Fig.5.3a, the ionic resistance of the sample prepared by using an interlayer coated on ETFE appears to be always lower by 5-9  $m\Omega cm^2$ , despite presenting a spike at lower current densities with a difference increase. Decreasing in ionic resistance at increasing current densities at the right side of the plot is usually associated with self-hydration, which is promoted as water formation at the cathode becomes increasingly fast. At EoT (Fig. 5.3b), the situation changes with a much higher spike arising for the sample prepared with the aid of ETFE foils. Since this characteristic behavior is found to be arising from the hydrocarbon membrane, as will be discussed in the following sections, its relevance could be explained as a higher exposure of sPPS:PBI-OO to the electrodes. Indeed, the difference between HFR at OCV and the minimum achieved across the whole polarization curve increases from 3.1  $m\Omega cm^2$  to 9.9  $m\Omega cm^2$ . Furthermore, the difference between ionic conductivity of the two samples at EoT is as well greatly reduced even outside the self-hydration region.



Figure 5.3: Comparison of HFR, measured at standard conditions at beginning (BoL) and end (EoT) of benchmarking protocol for CCMs prepared with sPPS:PBI-OO membranes and with interlayers originally coated on (a) Ammerflon® and (b) ETFE foils.

However, such small differences in ionic conductivity cannot justify the relevance of performance difference. For this reason, CVs collected were used to extrapolate the quantities reported in Fig.5.4 consisting of ECSA and H<sub>2</sub>-crossover current. This comparison allows to evidence that a modified preparation ap-



Figure 5.4: ECSA and H<sub>2</sub>-crossover current density extrapolated from CVss perfored at different steps of testing between CCMs using an interlayer prepared on Ammerflon® (*light blue*) or ETFE (*light green*).

proach leads to much higher active catalyst surface and also exhibits a lower gas crossover. A higher ECSA could be explained by different mechanics of the decal transfer attributable to lower stiffness and vertical interactions with the Nafion<sup>™</sup> interlayer by ETFE substrate, if compared to Ammerflon<sup>®</sup>. This allows to reduce flattening of the catalyst surface consequently improving the impregnation of catalyst layers, allowing a better reach of platinum particles by the polymer electrolyte, as shown in Figure 5.5. A reduced gas permeation can be due to the flatness of ETFE. In particular, the interface between carrier film and interlayer becomes the contact surface of impregnated electrodes and membrane. If this is uneven or patterned, pinching of the membrane might take place during lamination, locally (on the macroscopic scale) thinning the permeation path between anode and cathode. Studied samples have been observed with SEM to verify visually the differences between procedures. From these micrographs it was possible to measure the average indentation depth as the distance between a convolution of the protrusions and the valleys of the carbon particles. It is obtained that for thinner interlayers prepared on ETFE foil, the average indentation depth is  $180 \pm 40 nm$ , while for thicker interlayers coated on Ammerflon<sup>®</sup>, the same parameter is estimated to be  $42 \pm 9 nm$ . It appears clearly that both measurements are affected by a high error, this is due to the


Figure 5.5: FE-SEM micrographs collected from the interface between cathode catalyst and Nafion<sup>TM</sup> interlayer coated on (*top*) Ammerflon<sup>®</sup> and (*bottom*) ETFE after in situ testing with the benchmarking protocol.

irregular surface of catalyst layers. It is also noticed that the indentation depth of the interlayer coated in Ammerflon® is 4 times lower than the equivalent prepared on ETFE. Details of the indentation depth measurement are provided in Appendix C.

# 5.2 PROCESS OPTIMIZATION FOR INTERLAYER-LESS CCMs

First testing attempts were performed through the usual benchmarking route. However, all the CCMs couldn't survive through air starvation cycling of the conditioning procedure, as reported in Figure 5.6. This behavior was found to be odd since this procedureaimed to increase the performance of fuel cells rather than damaging them.

Since within the cathode catalyst layer of the CCM measured first there were residues of ethylene glycol and the result of this first attempt was not encouraging, a few variations were prepared as described Table 5.1. For this round of measurements, the process optimization protocol (Section 3.4.3) was adopted.

#### 5.2. PROCESS OPTIMIZATION FOR INTERLAYER-LESS CCMs



Figure 5.6: (a) Voltage (*blue*) and Current (*red*) tracked during conditioning cycles, the opacity of the line increases for each following cycle. (b) Voltage recorded during the high current density step of each conditioning cycle.

Sample name	Ionomer	$\mathbf{T}_{cal} \left[ ^{\circ} \mathbf{C} \right]$	<b>Residual solvent</b>	Preheating
Hot - EG	sPPS:PBI-OO	130	Yes, Ethylene Glycol	-
Reference	PFSA	130	No	4 min. at 150 °C
Hot - no EG	sPPS:PBI-OO	130	No	-
Cold - no EG	sPPS:PBI-OO	40	No	-
Cold - EG	sPPS:PBI-OO	40	Yes, Ethylene Glycol	-
Hot - no EG - Preheated	sPPS:PBI-OO	130	No	4 min. at 150 °C

Table 5.1: Summary table of the prepared CCMs for investigation of process parameters influence on performance and stability.  $T_{cal}$  refers to the temperature of calendering rolls for decal transfer.

#### 5.2.1 Behavior during conditioning cycles

Firstly, it was noticed that no measurements were possible from samples prepared according to the *Cold* - *EG* specifications. Subsequently, the same initial overview of the performance exhibited during conditioning was prepared for these samples, by tracking the potential achieved in the high current density step of each cycle. Resulting decays are plot in Figure 5.7 and a summary of relevant features can be found in Table 5.2.

As expected, *Reference* sample has negative decay due to the beneficial effect of conditioning on state-of-the-art fuel cells.

Unfortunately, this is not the case for any of the CCMs prepared with sPPS:PBI-OO membranes. In particular, sample *Hot* - *EG* is the worst performing, despite pre-



Figure 5.7: Comparison of the potentials achieved during high current density step of conditioning cycles.

senting the second lowest decay rate among the hydrocarbon-based CCMs. At the end of conditioning, all the other samples exhibit comparable performance. This allows to conclude that neither temperature, nor performing preheating before calendering leads to a tangible progress. Heating of assemblies is commonly exploited to overcome PFSAs glass transition temperature and favour mechanical adhesion among layers. Due to uncorrelation between processing temperature and performance, it can be speculated that mechanical contact between layers of a CCM is not critical for the effectiveness of a fuel cell. This remark is also consistent to the existence of Gas Diffusion Electrode (GDE) approaches in the realization of fuel cells, which consist in coating the GDL with an electrocatalyst layer, simply placed onto the membrane during assembly. Finally, it was decided to retain as standard procedure for future samples the route adopted for *Hot - no EG - Preheated* for its similarity with the preparation of reference samples. This decision is oriented to minimize the difference in conditions experienced by catalyst layers between reference and investigated fuel

#### 5.2. PROCESS OPTIMIZATION FOR INTERLAYER-LESS CCMs

Sample name	$\mathbf{U}_{1.3A/cm^2}^{before}$ [V]	$\mathbf{U}_{1.3A/cm^2}^{after}$ [V]	Decay rate [mV/cycle]
Hot - EG	0.536	0.366	7.9
Reference	0.721	0.736	-0.5
Hot - no EG	0.579	0.467	6.0
Cold - no EG	0.663	0.440	13.1
Hot - no EG -	0.658	0.446	12.1
Preheated		0	

Table 5.2: Summary of the performance at begin and end of conditioning. The decay rate was extrapolated through linear regression of the measured potential. $U_{1.3A/cm^2}^{before}$  is the potential recorded for the high current density step at the first cycle, while  $U_{1.3A/cm^2}^{after}$  is the same quantity at the last conditioning cycle.

cells, since no particular improvements could be obtained through modified procedures.

### 5.2.2 POLARIZATION CURVES

Sets of polarization curves were collected in two consecutive repetitions, even though the performance of these samples is highly dependent on the chosen lenght of the conditioning procedure, as shown in the previous section. These measurements were performed to evidence possible behaviors arising due to operation of the prepared fuel cells. Polarization curves collected in standard conditions with a serpentine flow field are reported in Fig. 5.8. It can be noticed that the *Reference* exhibits completely different performance to the one reported from the devices.

Meanwhile, all other samples exhibit mutual differences much smaller than compared to the *Reference*. Furthermore, these differences seem to thin down as the testing proceeds since the polarization curves appear to be more spread at Begin-of-Life (BoL) than for End-of-Test (EoT).

All the polarization curves collected for *Hot - no EG - Preheated* are reported in Fig. 5.9a. It can be seen that performance exhibited during the second set of polarization curves is only slightly lower than the first set, except for what observed in CW conditions. This allows to conclude that performance loss due to operation is not particularly relevant, especially in comparison to the efficiency difference with the reference.

Another interesting aspect consists in the inverse relation between relative humidity and efficiency. Indeed, in CW with 100 % RH, is exhibiting the lowest



Figure 5.8: Comparison of the polarization curves collected in Standard conditions at (a) BoL and (b) EoT using the process optimization protocol.

I-V curves, while the best ones are represented by the measurements at HD conditions with 30 % RH. This result can be explained by the water retention properties of the sPPS:PBI-OO membranes. *Sulfonated polyphenylene sulfones* possess a higher IEC and more open nanomorphology compared to PFSAs. These properties lead to stronger correlation between  $\lambda$  and relative humidity. Presence of abundant free water is ultimately responsible for the soaking of catalyst layers and GDLs resulting in an increased resistance to the diffusion of gaseous O<sub>2</sub> toward the catalytic sites.

### 5.2.3 HFR

Contestually to the collection polarization curves, also ionic resistance across the membranes is measured. Also in this case the measurements reported are only the ones referring to the sample *Hot- EG - Preheated* since relevant differences could not be highlighted across the discussed alternative routes.

In Figure 5.9b, it can be appreciated that no relevant difference of HFR is detectable between homologous conditions in the two sets of measurements. An especially relevant feature of the sPPS:PBI-OO membrane is arising in HD conditions at low current densities and consists in a repentine increase in ionic resistance as current density decreases. Such behavior can be explained by a lower acidity of sulfonate groups within sPPS when compared to PFSA. If the acidic functions of an ionomer are not sufficiently strong, under especially dehydrating conditions it might happen that complete dissociation cannot take



Figure 5.9: (a) Polarization curves and (b) HFR measured from the sample *Hot* - *no EG* - *Preheated*.

place, reducing the effective IEC available for protonic transport. However, during operation of a fuel cell, water is produced as the cathode side proportionally to the generated current. Therefore, hydration state of the fuel cell, especially the membrane, is not simply a result of the thermodynamical equilibrium with its environment but is determined by its operating conditions.

Additionally, ionic resistance seems to be lower in standard than CW conditions. Nevertheless in both cases the obtained value is between 40  $m\Omega$   $cm^2$ and 30  $m\Omega$   $cm^2$  which highlights essentially two important milestones in the development of proton exchange membranes. Firstly, the ionomers used within these fluorine-free materials possesses a satisfying degree of ionic conductivity. Secondly, to obtain such an advanced conductiveness it is necessary to have reached an high degree of maturity with respect to the processing of ionomer and reinforcement. As a matter of fact, a good impregnation of pores within the reinforcement by ionomer solution has to be achieved since the former is not an intrinsic ionic conductor.

# 5.3 NAFION<sup>TM</sup> INTERLAYER EFFECT ON CCMs with PFSA MEMBRANES

The effect of Nafion<sup>™</sup> interlayers in CCMs based on PFSA membranes was investigated preliminarly through the conditioning protocol (Section 3.4.4). Goal of this comparison is to identify the plausible effects of interlayers and possibly

refine the subsequent evaluations of sPPS:PBI-OO membranes.

### 5.3.1 POLARIZATION CURVES

Collected polarization curves all show the same difference between the two samples. As can be seen in Figure 5.10a it appears that the sample prepared with additional interlayers presents anticipated mass transport losses which lead to a deficit in performance growing exponentially with current density.

Through this technique, it was also possible to determine that conditioning doesn't lead to a degradation in performance for both samples. The overview over all these measurements is reported solely for the CCM with Nafion<sup>™</sup> interlayers. As a side note, a small improvement is observed even with the shortened conditioning procedure adopted, consisting of 20 cycles rather than the 120 used for benchmarking. Nevertheless, mass transport limitations are the first cause



Figure 5.10: (a) Comparison between CCMs based on Gore SELECT membrane with and without Nafion<sup>TM</sup> interlayer at HD conditions. (b) Comparison of all the polarization curves collected from a CCM with Gore SELECT membrane and interlayers placed on the inner side of the electrodes.

of capping in the power output and such an effect is exemplarly displayed by the two samples discussed in this Section. A comparison of the maximum power output at all the stages of testing is reported in Figure 5.11. The loss in power output appears to be rather consistent with an average of 13.7  $\pm$  1.4%.

Lastly, from the polarization curves it was possible to prepare Tafel plots to highlight the activation region at low current densities (see Fig. 5.12). From this

### 5.3. NAFION™ INTERLAYER EFFECT ON CCMs WITH PFSA MEMBRANES



Figure 5.11: Maximum power output comparisons between samples with and without interlayers applied between electrodes and state-of-the-art membrane.

plot it appears clearly an overlap of the two curves. Therefore, the additional layer and processing required for its application do not modify catalyst activity.



Figure 5.12: Tafel plot comparisons between samples prepared with Gore SE-LECT membranes with (light blue) and without (light green) Nafion<sup>™</sup> interlayers. Data shown is rielaborated from the polarization curve acquired in standard conditions after conditioning.

### 5.3.2 HFR

It is found that the addition of interlayers to a state-of-the-art CCM leads, as expected, to an increase in ionic resistance due to the longer path separating the two electrodes. It is observed that in standard and *Cold* & *Wet* conditions, difference in proton conductivity is rather stable independently from the current density circulating through the fuel cell, as depicted in Figure 5.13a. However, in *Hot* & *Dry* conditions the difference in ionic resistance is less stable and possibly greater at lower current densities. This is easily attributed to the different EW of interlayer and membrane. Indeed, the PFSA membrane has an EW of 765 g/mol while the Nafion<sup>TM</sup> used, possesses a 1100 g/mol. Among PFSA compounds, a lower equivalent weight increases the water retention properties, ultimately resulting in better hydration in dry conditions.



Figure 5.13: Comparison of ionic ASR between CCMs based on Gore SELECT M765.08 membrane with and without Nafion<sup>TM</sup> interlayers at (a) *Cold* & *Wet* and (b) *Hot* & *Dry*.

Nevertheless, in HD conditions, ionic resistance shows a steep variation at low current densities. For this reason, even small variations in self-hydration properties lead to unreliable estimation of the difference between these two samples. For this reason the additional term of HFR due to the interlayer had to be calculated exclusively from the measurements in the first two conditions discussed, Standard and CW. The weighted average resistance of a single interlayer was found to be  $R_{i,IL} = 0.38 \pm 0.09 \ m\Omega \ cm^2$ .

# 5.3.3 Cyclic Voltammetry

Cyclic voltammetries were collected before and after each set of polarization curves with the intent to characterize the catalyst evolution across testing. The first CV is collected before any operation or conditioning of the CCM and therefore allows to identify the activation state of the catalyst as-prepared. This measurement applied to the two samples discussed in this Section is reported in Fig. 5.14.



Figure 5.14: Cyclic voltammetries collected from CCMs with and without interlayers on top of a Gore SELECT membrane at Begin-of-Life (BoL).

Two differences are clearly evident from this graphs. *ECSA* for the sample with interlayer is noticeably lower, while the opposite is true for the crossover current. This speculation is supported by the fact that this CCM shows a smaller anodic double layer current but an almost identical one in the cathodic scan. Furthermore, is it possible to identify at least one peak at around 0.65 *V* which is absent for the sample without interlayer, whose exact attribution is not clear but certainly shows a contamination of the catalyst nanoparticles.

Nevertheless at the end of test (EoT), effect of contamination disappeared, as reported in the left panel of Figure 5.15. Within the right panel of the same, it is shown that activation of the catalyst in presence of the interlayer has taken place throughout the test, eventually reaching a comparable value to its counterpart. Nevertheless, hydrogen crossover current seem to remain lower in the sample with interlayer. This is attributed to the better gas barrier effect offered by a thicker polymer layer and is therefore not surprising.



Figure 5.15: Cyclic voltammetries collected from CCMs with and without interlayers on top of a Gore SELECT membrane at EoT. On the right panel, relevant parameters extracted at different stages of testing are summarized.

# 5.4 NAFION<sup>TM</sup> INTERLAYER EFFECT ON CCMs with sPPS:PBI-OO membranes

Subsequently, the effect of Nafion<sup>™</sup> interlayers was investigated on CCMs with sPPS:PBI-OO membranes. In order to obtain further insights on the initial observation of repentine performance loss, also a sample was prepared with an interlayer at the sole cathode side.

### 5.4.1 POLARIZATION CURVES

The polarization curves collected with the mentioned samples and reported in Figure 5.16a allow to distinguish a marked difference in performance between samples possessing at least an interlayer at the cathode compared to the sample who doesn't have such layer. Interestingly, performance of samples with IL at both sides and only at cathode sides is overlapping at low-medium current densities and they only depart from each other in the mass transport limitation region, where water backdiffusion to the anode becomes a relevant phenomena. However, after undergoing conditioning cycles, the situation changes radically (Fig. 5.16b). As a result, the performance of samples not possessing any interlayer on the anode side deteriorated, in contrast with the behavior shown by the sample with interlayers on both sides. Looking more in detail the activa-



Figure 5.16: Polarization curves collected for CCMs prepared with IL at both electrodes, only on the cathode or neither side. The reported measurements have been performed in Standard conditions at (a) BoL and (b) EoT.

tion region, it becomes clear that the absence of Nafion<sup>TM</sup> interlayer over the cathode leads to worsened reaction kinetics, linked to the Tafel plot slope. The corresponding overview is reported in Figure 5.17 and allows to ascertain that kinetics of the sample with IL at the cathode is affected only lightly by conditioning, since its Tafel plot is still parallel to the sample characterized by ILs on both sides, especially at  $j_{ECSA} < 1 \ mA \ cm^{-2}$ .

Therefore, performance losses at the anode side are not linked to worsened kinetics. However, it must also be kept in mind that overall kinetic overpotential is mainly driven by the cathodic reaction, due to the acidic conditions of PEM-FCs. This implies that even relatively broad losses of anodic reaction kinetics leads to exceedingly low increase of the overall kinetic overpotential.

By reporting the maximum power output of each polarization curve (Fig. 5.18)



Figure 5.17: Tafel plots for CCMs prepared with IL at both electrodes, only on the cathode or neither side. The reported measurements have been performed in Standard conditions at (a) BoL and (b) EoT.



Figure 5.18: Maximum power output for each polarization curve performed within the Conditioning protocol (Section 3.4.4). Samples reported in this bar chart are all prepared with an sPPS:PBI-OO membrane but differ for the Nafion ® demark interlayers added on both electrodes, solely at the cathode or on neither sides.

The main observation that can be taken away from this overview consists in the generalized performance loss for both the samples not possessing interlayers at both electrodes across the conditioning step, which takes place after HD BoL and before Standard (Std) EoT. The next subsection is therefore focused to provide an insight into the behavior of these samples during conditioning.

### 5.4.2 Behavior during conditioning

Also in this case, *U* is tracked at each cycle for the high current density step and represented in Fig.5.19 along with the linear regression extrapolated from the first 10 cycles.



Figure 5.19: Potential achieved at each conditioning cycle by CCMs with ILs at both electrodes (*light blue*), only at the cathode side (*fuchsia*) and at none of the membrane faces (*light green*).

Resulting measure of the decay rate is reported in Table 5.3 and shows an attempt to quantitatify the protective effect played by Nafion layers. Indeed, decay rate for the sample with interlayer at the sole cathode is somewhat in between the value extrapolated for the other samples. This points that decay effect is taking place simmetrically at cathode and anode in comparable amounts.

Sample name	$U_{1.3A/cm^2}^{before} [V]$	$\mathbf{U}_{1.3A/cm^2}^{after}$ [V]	<b>Decay rate</b> [mV/cycle]	Recovery [%]
with ILs	0.701	0.715	-1.1	-
with IL at cathode	0.567	0.513	5.2	14
without ILs	0.401	0.326	9.3	16

Table 5.3: Summary table of the decay observed in samples distinguished by the placement of Nafion<sup>TM</sup> interlayers. Potential at the high current density step is reported for the first and last cycle available. A linear regression is obtained from the points collected in the first 10 cycles and is used to calculate the decay rate and the recovery of performance observed after potentiostatic hold at 0.35 V.

Another notable feature is the partial recovery happening after the potentiostatic hold at 0.35 V for 5 minutes following the  $10^{th}$  cycle. This effect is quantifiable as the difference between projected regression and measured  $13^{th}$ cycle, normalized by the difference between expected potential and the value measured for the sample with both interlayers:

$$Recovery[\%] = \frac{\bar{U}_{1.3A/cm^2}^{13} - U_{1.3A/cm^2}^{13}}{\bar{U}_{1.3A/cm^2, ref}^{13} - \bar{U}_{1.3A/cm^2}^{13}}$$
(5.1)

Where  $\bar{U}_{1.3A/cm^2}^{13}$  is the measured potential at the 13<sup>th</sup> cycle,  $U_{1.3A/cm^2}^{13}$  is the same quantity but obtained from linear extrapolation of the first half of conditioning and  $\bar{U}_{1.3A/cm^2,ref}^{13}$  corresponds to the measured potential from the sample with interlayers on both sides at the same conditions. 11<sup>th</sup> and 12<sup>th</sup> cycle were discarded due to their tendency of being outliers. Particularly, it emerges that relative recovery of performance is very similar between the two samples. However, the formulation of an hypothesis for this phenomena will require more systematic experiments.

### 5.4.3 Galvanostatic EIS

Galvanostatic EIS as described in Section 3.4.4 were collected and their results are indicative of the profoundly different behavior of the anode kinetics taking place in CCMs without Nafion IL. In such conditions, the expected spectroscopy should be exhibiting ionic resistance through the cathode electrode and therefore should be well modeled by the equivalent circuit in Figure 3.5b. Eventually, this behavior is observed for the CCM with both ILs as depicted in Fig.5.20.

On the contrary, for samples without interlayer at the anode, a semicircle associated to anodic reaction was visible, as in Figure 5.21.

This suggests that kinetics of the HOR is significantly halted in absence of an interlayer. To confirm this difference, the collected data has been fit through the described models and in both cases the model choice can be recognized as appropriate. The model considering protonic conduction within the cathode catalyst layer has been nicknamed *TLMQ*, while the alternative considering faradaic processes at the anode has been renamed *Anode*. Nevertheless, it was not possible to describe the cathodic reaction with *TLMQ* model due to a limitation of the software package used for these analysis. The three samples have been compared with each other to highlight their different behavior at low and high



Figure 5.20: Galvanostatic EIS collected after half conditioning procedure from CCMs based on sPPS:PBI-OO membranes with additional Nafion<sup>™</sup> ILs.



Figure 5.21: Galvanostatic EIS collected after half conditioning procedure from CCMs based on sPPS:PBI-OO membranes without additional Nafion<sup>™</sup> ILs.

frequency, respectively on the upper and lower left in Figure 5.22.

Representation of the full spectrum allows to recognize that LFR differs among samples. In particular, a reduction in number of interlayers is associated with increases in radius. For this reason, the full spectra have been modeled and the area-specific resistance describing the low frequency feature ( $ASR_{LFR}$ )



Comparison of EIS spectra from Reference CCM + ILs after cond

Figure 5.22: Complete Galvanostatic EIS spectra collected after conditioning procedure for sample with different interlayer configuration. On the upper left, the complete spectras are shown, while on the bottom left a Nyquist plot magnifying on the high frequency features is reported.

has been tracked across the procedure, results are shown in Figure 5.23.



Figure 5.23: Progression of the resistance associated to the low frequency semicircle fit through *Anode* model and compared among samples. The lines correspond to the percent increase with respect to the sample with both interlayers

All CCMs experience an overall reduction of  $ASR_{LFR}$  across conditioning, but relative difference of samples without anodic interlayer monotonously increases. Since a feature of the anode electrode cannot possibly influence cathodic kinetics, it can be speculated that anodic mass transport component of  $ASR_{LFR}$ is eventually another property being affected by conditioning. Lastly, it can be

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noticed from the bottom left plot of Figure 5.22 that radiuses of high frequency semicircle differ between samples with a single or no interlayers. Also the progression of this property is represented in the for of a bar chart with a line representing the percent difference among the samples.



Figure 5.24: Progression of the resistance associated to the high frequency semicircle fit through *Anode* model and compared among samples. The line corresponds to the percent increase with respect to the sample without interlayers

It is clearly observed a relative increase of  $ASR_{an}$  for the sample with only one interlayer when compared to the CCM without any of them. Considering that mass transport at the anode is aided by thin electrodes, purity and fugacity of the reactant, this suggests that presence of cathodic interlayer indeed has a negative influence on the kinetics of HOR. All these found correlations support the idea that a Nafion<sup>TM</sup> IL acts as a chemical barrier, halting the leaching of poisoning species from within the membrane to reach the catalyst. Therefore, it appears that placing such barrier layer at the cathode side speeds leaching at the anode side. This behavior would also explain why the decay rate found for this sample is slightly higher than half of the decay rate for the CCM without interlayers. However, it will be important to evaluate EIS measurements also at different current densities to better descriminate  $ASR_{LFR}$  into its cathode kinetic,  $ASR_{ct,cat}$ , and mass-transport,  $ASR_{mt,cat}$ , components.

### 5.4.4 HFR

Measurement of ionic resistance across the membrane does not provide particularly unforeseen insights (Figure 5.25). Also in this case, it is observed that the addition of interlayers leads to the increase of ASR and that in HD conditions, dehydration leads to a loss of conductivity. Unexpectedly, HFR measured from the sample with Nafion<sup>™</sup> IL at the cathode is tendentially higher than the corresponding measure for the sample with both ILs.



Figure 5.25: HFR measurements collected during polarization curves at Beginof-Life of the sample in (a) Standard and (b) Hot & Dry conditions.

The partly interlayered sample appears to exhibit an unexpectedly high ionic resistance especially at low current densities. Unfortunately it is not possible to appoint an explanation to this observation for the time being.

# 5.4.5 Cyclic Voltammetry

To characterize the cathode electrodes, CVs has been performed before and after I-V curves sets preceding and following conditioning procedure, obtaining a total of four measurements for each sample. It is possible to assess the initial state of health for these samples by comparing the CVs collected first. It is immediately recognizable that the CCM with cathode interlayer presents the highest hydrogen absorption/desorption peaks, in decreasing order followed by the sample with both interlayers and ultimately the one without. At first sight, this difference in cathodic property among the samples prepared with IL at this electrode might be surprising.

However, the observation can be explained by the fact that successful lamination of interlayer-less CCMs based on sPPS:PBI-OO membranes require a higher level of compression compared to the counterpart with interlayers, specifically 80  $\mu$ m against 30  $\mu$ m. Therefore it is possible that at the first utilization of a fuel cell without prior activation, this fundamental difference in preparation might



Figure 5.26: Comparison of the first CV collected from each sample. Curves are the average resulting from the last three cycles of each measurement

play a role. Nevertheless, as was observed in Figure 5.4, even small processing modification can play a major role in determining initial activation of an electrocatalyst.

Furthermore, it is also understood through these CVs that various contaminations might be present within the cathode catalysts of all CCMs due to the presence of unexpected peaks in the potential window 0.3 V - 0.7 V. To evaluate the catalyst layer after conditioning, the corresponding CVs are reported in Figure 5.27.

At this stage, samples with a cathode interlayer present remarkably overlapping features, essentially proving that cathode catalyst is unaffected by testing and conditioning. However, opposite situation is found for the CCM prepared without interlayers. Firstly, the activated catalyst seems to be 50 % less than other samples, suggesting heavy poisoning of platinum nanoparticles. An attempt to estimate the amount of leached poisoning species and their penetration is reported in Appendix D. Secondly, a redox system is observed in the double layer region indicative of the redox activity of contaminants. However, such peak is too shallow and broad to reliably extract relevant parameters. Finally, it is observed that all samples exhibit a very low H<sub>2</sub> crossover current which is indicative of membrane integrity and homogeneity.



Figure 5.27: (*left*) Averaged cyclic voltammetries after conditioning. (*right*) Evolution of relevant parameters across testing.

Material	Vibrational mode	Wavenumber [cm <sup>-1</sup> ]
	Asymmetric C-H stretching	(2915)
PE	Symmetric C-H stretching	2845
	CH2 Scissoring	(1465)
Water	O-H scissoring	1630
sPPS	S=O stretching in $-SO_2-$	1150
	S=O stretching in $-SO_3$	1050
PBI-OO	N-H stretching	(3250)

Table 5.4: Most prominent vibrational modes expected from each material composing sPPS:PBI-OO membranes. Vibrational modes whose position is placed within brackets have not been measured. Reason for this is the redundancy of PE signals and the low intensity of the peak compared to the background for PBI-OO.

# 5.4.6 ATR-FTIR

To investigate the possible chemical degradation of sPPS:PBI-OO membranes, ATR-FTIR spectroscopies were collected and analyzed exclusively with respect to few diagnostic peaks, due to the placement of most signals within the fingerprint region  $(1300cm^{-1} \text{ to } 500cm^{-1})$  and the overlap of signals from multiple materials. These features a consist of the peaks listed in Table 5.4.

This technique was applied on CCMs based on sPPS:PBI-OO membranes prepared with and without Nafion<sup>™</sup> interlayers. After testing with the Conditioning Protocol, the catalyst layers and eventually also the interlayers were

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removed with a 1:1 mixture of 1-propanol and ethanol by scrubbing with a dust-free napkin. Afterwards, the cleaned membranes were left to dry overnight before proceeding to the measurements. These samples have been characterized within the active area and outside of it, to isolate the effect of testing from possible influences coming from the cleaning procedure. Also the pristine membrane was characterized through this technique to evidence possible differences arising due to handling, lamination as well as exposure to moisture and relatively high temperature as in the sample holder during testing. In an effort to improve readability of the obtained plots, all the peaks have been normalized by the peak attributed to  $-SO_3$ , located at around  $1050 \text{ } cm^{-1}$ . Since ATR-FTIR spectroscopy is a technique particularly sensitive to the sample's surface and given the thickness of membranes employed for this study (5  $\mu m$  to 10  $\mu m$ ), multiple measurements were performed in every point since local defects could lead to unrepresentative spectras, as shown in Figure 5.28.



Figure 5.28: Repeated ATR-FTIR spectroscopy from a CCM based on sPPS:PBI-OO in spots belonging to the active area of the sample, cleaned after testing.

Especially the signal ratio  $SO_3/PE$  is particularly sensitive to local thinning of the sPPS:PBI-OO overlayer covering the impregnated PE reinforcement due to the surfacial nature of ATR signal. Therefore, for further evaluation and comparison, only the reproducible spectras were used while the outlying ones were discarded. The effect of aging (or testing) is clearly visible from comparison of the pristine membrane with portions of the membrane which were active during testing. By adding in the same comparison also measurements collected from the inactive area of the fuel cell, it is also possible to see that signals associated to PE reinforcement are absent within the pristine material, but then are accentuated by cleaning and finally register a steep increase after aging.



Figure 5.29: Comparison ATR-FTIR spectroscopies from the cathode side of an sPPS:PBI-OO membrane to evidence effects of cleaning and aging.

This can be associated to a thinning of the ionomeric layer covering the reinforcement as well as a reduction in the impregnation of pores within PE. Furthermore, an increase of the signal placed at 1150  $cm^{-1}$  can find two possible interpretations. Desulfonation of the phenyl rings is the most likely, or also reductive cross-linking might take place. Cross-linking of sPPS might take place through the sulfonate groups, which in reductive conditions might establish a sulfone bridge connecting polymeric chains. This last mechanism would lead to the conversion of  $-SO_3$  moieties into  $-SO_2-$ .

To investigate the relation existing between performance retention and presence of interlayers, the ATR-FTIR spectra collected from the active areas of both samples have been compared in Figure 5.30 and the relative intensities of relevant peaks listed in Table 5.5.



Figure 5.30: Comparison ATR-FTIR spectroscopies from the active areas on both sides of sPPS:PBI-OO membranes belonging to samples tested with and without interlayers.

It is important to remark that spectras collected from the cathode sides of

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both CCMs are more similar then anode side spectras. The most prominent features supporting this statement are the vibrational modes assigned to PE at 2845  $cm^{-1}$  and 2910  $cm^{-1}$ .

			Moiety			
	Site	Repetition	SO3	SO2	O-H	C-H
	Pristine	1	1.00	1.07	0.45	0.25
	Cathode not active	1	1.00	1.17	0.50	0.39
sPPS:PBI-OO		1	1.00	1.18	0.37	0.47
	Cathode active	2	1.00	1.22	0.37	0.59
		3	1.00	1.30	0.35	1.00
	Anode active	1	1.00	1.29	0.30	1.63
sPPS:PBI-OO	Cathode active	1	1.00	1.25	0.35	0.94
with ILs	Anode active	1	1.00	1.16	0.36	0.40

Table 5.5: Measured peak intensities from samples shown in the figures reported.

It can be argued that the anode seems to be the most affected electrode by the absence of interlayers, showing a relevant difference in  $C-H/SO_3$  ratio between the two samples. Such ratio is 1.64 and 0.4 for *sPPS:PBI-OO* and *sPPS:PBI-OO* with ILs, respectively.

### 5.4.7 SEM

SEM micrographs were acquired from polished cross-sections of tested CCMs in order to observe the samples and measure if membrane thinning occurs, as reported in Figure 5.31. Measured thicknesses are listed in Table 5.6.



Figure 5.31: SEM micrographs of the CCMs based on sPPS:PBI-OO membrane (a) without and (b) with Nafion<sup>™</sup> interlayers on both sides.

In both SEM micrographs it is possible to recognize the structure of a CCM. The top bright layer corresponds to the cathode catalyst layer, underneath which are placed the electrolytes. Interlayers can be recognized due to their smooth appearance with a shade of grey somewhat intermediate between catalyst layers and membranes. The darker layer in the middle consists in the membrane including its reinforcement.

However, with the secondary electrons signal it is not possible to distinguish the inner layers of the membrane. For this reason the reinforcement has been observed through the AsB detector as reported in Figure 5.32. After repeated measurements, the reinforcement appears to be  $4.4 \pm 0.2 \ \mu m$  thick, compatibly with manufacturer's specifications.



Figure 5.32: SEM micrograph collected through AsB detector to evidence the slightly lighter reinforcement layer within a CCM based on sPPS:PBI-OO membrane with interlayers on both electrodes. Brightness and contrast were adjusted to make more evident the layer within the membrane, but placement is identical to previous SEM micrographs.

From the thickness of different layers it is understood that testing doesn't lead to significative membrane thinning, even in absence of Nafion interlayer. Also, from the above micrographs, it is not possible to identify visible differences between membranes in CCMs with and without interlayers. Therefore, the source of observed performance loss cannot be attributed to membrane chemical decomposition. SEM micrographs couldn't lead to distinguish a difference between the samples based on the presence or lack of interlayers as was established from ATR-FTIR spectroscopies. However, it is important to remind that aged samples had to be cleaned of any catalyst layer residuals before the collection of spectroscopies. Therefore, it is possible that during the cleaning, soluble species might have been asported if they concentrated at the membrane's surface.

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	<b>Thickness</b> [ $\mu m$ ]			
Element	sPPS:PBI-OO without ILs	sPPS:PBI-OO with ILs		
Cathode catalyst layer	9.9 (0.3)	10.88 (0.16)		
Cathode interlayer	-	1.09 (0.12)		
Membrane	8.5 (0.2)	8.7 (0.2)		
Anode interlayer	-	0.63 (0.06)		
Anode catalyst layer	2.50 (0.15)	3.39 (0.15)		

Table 5.6: Thickness measurements obtained from SEM micrographs in Figure 5.31.

Followingly, micrographs from cryogenically broken CCMs were collected by using a FE-SEM to obtain clearer details of the materials thanks to the higher accessible magnifications. With this technique it was possible to observe the interface between catalyst layer and ionomers.



Figure 5.33: FE-SEM micrographs showing the catalyst-ionomer interface when the ionomer is (a) Nafion<sup>TM</sup> or (b) sPPS:PBI-OO.

As can be seen in Figure 5.33, both ionomers seem to bind properly with the catalyst layer as no gaps could be found. This observation reinforces the idea that mechanical contact is not the issue of samples prepared without the use of an interlayer. However, in some locations of the CCM without interlayer, some defects were observed as reported in Figure 5.34a.

Since these defects appear to be visible on both sides, it is clear that they cannot be due to catalyst layer preparation. Rather, they might form during the lamination or testing of the CCM. In any case, increasing the magnification (Figure 5.34b) allows to identify the formation of bigger cavities within the catalyst layer and presence of ionomer patches which are otherwise absent.



Figure 5.34: FE-SEM micrographs of a defective site at different magnifications: (a) 5kX and (b) 25kX.

This observation seem to confirm that testing might lead to the mobilization of polymer electrolyte from within the membrane which could be transported by water into the electrodes, possibly disrupting the porous microstructure of the latter. However, it is not clear how a phenomena that seems to be localized might influence the whole device in terms of performance. For the sake of completeness, it is also noted that the membrane appears to be much thinner than what previously measured, having a thickness of only  $1.39 \pm 0.12 \ \mu m$ . Nevertheless, it must be said that measuring thicknesses from cryogenically broken samples is not recommended due to the uneven topology of the cross-sections and possible plastic deformations occurring as a result of the breakage.

# 5.5 Differential cell testing

A differential setup was used to replicate the performance loss observations and possibly apply additional techniques made available by the stricter control in operating conditions of the CCMs during testing. In this configuration, only two samples were tested consisting of CCMs based on sPPS:PBI-OO membrane. One sample had Nafion<sup>TM</sup> interlayers between the electrolyte and each electrode, while the other was prepared without. For simplicity, they will be named in this section as *sPPS:PBI-OO with ILs* and *sPPS:PBI-OO*, respectively, to ease the reading. In order to minimize the discrepancies among samples, both were prepared using the same sheet of membrane.

#### 5.5. DIFFERENTIAL CELL TESTING

### 5.5.1 POLARIZATION CURVES

Polarization curves were collected for these two samples according to the specifications in Section 3.3.1 before (BoL) and after (EoT) applying the complete conditioning procedure. Sample *sPPS:PBI-OO* couldn't survive the break-in step, causing a system shut-down after 96 cycles during the night. Tests for evaluating the sample after conditioning were performed the following day. The measurements are reported in parallel figures for each sample in Figure 5.35.



Figure 5.35: Polarization curves measured with differential setup configuration with samples (a) *sPPS:PBI-OO with ILs* and (b) *sPPS:PBI-OO*.

Firstly, it is still noticed that in absence of interlayers performance is negatively affected by conditioning, since curves recorded after, in darker colors, are worse compared to the ones collected before (lighter colors). Meanwhile the procedure turns out to have no negative effect for sample *sPPS:PBI-OO with ILs*. Secondly, it is important to highlight the good performance achieved in the *O2* curves by *sPPS:PBI-OO with ILs*. This measurement can be appointed as a benchmark for the future development of sPPS:PBI-OO membranes, once these performance losses will be solved. For both samples, the worst performance is recorded in HD conditions as also displayed in Figure 5.36. A reason may be found in the ionic resistance, which increases abruptly in drier conditions. From this overview of  $P_{max}$  it is observed that the performance difference in Std, HD and CW conditions doesn't change significantly between before and after conditioning. This could depend on the fact that during collection of the HD curve, in this setup and with state-of-the-art PFSA-based fuel cells it is usually



Figure 5.36: Maximum power output comparison for all steps of testing between *sPPS:PBI-OO with ILs* and *sPPS:PBI-OO*. The green line corresponds to the relative performance lost due to the absence of Nafion<sup>TM</sup> interlayers.

observed sulfonate adhesion to Pt, reason why a dedicate recovery protocol is put in place following these harsh conditions (Appendix B.1). However, since contamination of the catalyst has already been ascertained, it is possible that contaminant species irreversibly react with the nanoparticles causing a stable loss of electroactive area.

# 5.5.2 HFR

Measurement of ionic resistance from these samples returns values comparable with findings from previous sections. However, due to the completely dry gas flow and the short path, self-hydration becomes much less favoured, reason why in HD conditions the ionic resistance increases dramatically for sPPS:PBI-OO membranes, as reported in Figure 5.37.

The fact that even at relatively high current densities, the ionic resistance persists above 100  $m\Omega$   $cm^2$  is indicative of the low water retention capabilities of sPPS:PBI-OO membranes in severely dry conditions. This matter should be addressed carefully since one of the key points in favour of hydrocarbon ionomers is their operability at higher temperatures.

### 5.5.3 Cyclic Voltammetry

Also in this iteration, a markedly different evolution of the catalyst was found in CVs collected before any procedure and after conditioning. Such comparison can be seen in Figure 5.38.

In this case, both samples were laminated with the similar compression

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Figure 5.37: HFR measurements in *Hot & Dry* conditions with *sPPS:PBI-OO with ILs* and *sPPS:PBI-OO* CCMs.



Figure 5.38: CVs collected at (a) BoL and (b) after conditioning (EoT) for samples *sPPS:PBI-OO with ILs* and *sPPS:PBI-OO*.

80  $\mu$ *m* and exhibit almost identical CVs at BoL. Nevertheless, lack of ECSA and contamination is found once more for *sPPS:PBI-OO* at End-of-Test (EoT).

### 5.5.4 Galvanostatic EIS

An advantage of differential setup is the possibility to obtain reliable galvanostatic EIS at all current-set points of the polarization curves. From the analysis of impedance spectra obtained this way it is possible to model the electrochemical parameters, in this case through the *TLMQ* model. For compactness, only the data derived from *O2* polarization curves are reported. The reason why these are to be preferred against the others, consists in the fact that temperature and relative humidity conditions should prevent water condensation within the fuel cell. Furthermore, high partial pressure and flow of  $O_2$  minimizes gas transport limitations. In Figure 5.39, all extrapolated resistive parameters are reported.

With respect to HFR and  $ASR_p$ , it can be seen that *sPPS:PBI-OO with ILs* undergoes marginal but consistent improvement. For the same sample,  $ASR_{LFR}$  is substantially overlapping between BoL and EoT in the low current density regime. Above 1  $A cm^{-2}$  two distinct behaviors are seen. Before conditioning the sample hits a delayed but more abrupt deviation from linearity. After conditioning such deviation is more gradual and eventually leads to monotonously decreasing trend. This underlines essentially a reduction in mass transport limitations as a result of conditioning. For *sPPS:PBI-OO*, all extracted parameters



Figure 5.39: Regression results of Galvanostatic EIS measurements in O2 conditions for *sPPS:PBI-OO* and *sPPS:PBI-OO* with ILs before and after conditioning. The plots shown report values of: (a) HFR, (b)  $ASR_p$  and (c)  $ASR_{LFR}$ .

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increase across conditioning. However, difference between the two samples can be evidenced by reporting the difference in overpotentials among them before and after conditioning, as reported in Figure 5.40. Overpotentials can be obtained by the integration of area-specific resistance plots as a funciton of the current density. Difference in overpotentials is obtained at BoL and EoT through the subtraction of  $\eta$  calculated for *sPPS:PBI-OO with ILs* from  $\eta$  for *sPPS:PBI-OO*. From this plot it becomes clear that ionic conductivity plays an almost negligi-



Figure 5.40: Overpotential difference extrapolated for each area-specific resistance contribution.

ble role in the determination of performance difference and degradation. The extra overpotential ( $\Delta \eta$ ) which grows the most across conditioning is  $ASR_p$ , associated to the protonic conduction within the catalyst layer. However, the most relevant difference between the two samples is found to be on  $ASR_{LFR}$ , even if this difference doesn't seem to grow particularly across conditioning. A possible explanation for this last finding may reside on the fact that during the collection of polarization curves water transport is directed towards the cathode, leading possible contaminants into this electrode. Meanwhile, conditioning inverts water net mass flow repeatedly, possibly causing the contamination of both electrodes equally. According to this explanation, it could be argued that a more relevant relative increase in  $ASR_p$  than  $ASR_{LFR}$  could be explained since the for-

mer is subsceptible of both electrodes, while the latter is carrying information exclusively related to the cathode.

Furthermore, it is possible to isolate within  $ASR_{LFR}$  the contributions due to reaction electrochemical activation losses and mass transport limitations through the linearization of  $\eta_{LFR}$  at low current densities, below 1  $A cm^{-2}$ , as reported in Fig.5.41. To do so, it is necessary to plot current density with a logarithmic scale. As also highlighted in Table 5.7, presence of interlayers leads



Figure 5.41: Linearization of  $\eta_{LFR}$  for *sPPS:PBI-OO* and *sPPS:PBI-OO* with ILs before and after conditioning

substantially to a reduction on the intercept of such linearization, but doesn't affect the regression's slope.

Sample	slope [mV/dec]	intercept [mV]
no ILs - BoL	99 (4)	280 (4)
no ILs - EoT	110 (5)	290 (5)
with ILs - BoL	97 (4)	233 (4)
with ILs - EoT	102 (4)	239 (4)

Table 5.7: Regression parameters for linearization of  $\eta_{LFR}$ .

Such difference can be explained due to different ECSA. Considering that

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ECSA for *sPPS:PBI-OO with ILs* is 2 times the one of *sPPS:PBI-OO* ( $k_{ECSA} = 2$ ), the resulting traslation on the *y-axis* due to current normalization would be expressed as:

$$\delta\eta = \frac{slope}{k_{ECSA}} \approx 50mV \tag{5.2}$$

Corresponding to the difference in intercept between the samples. Nevertheless, all the plots seem to depart from linear regime over  $1 A cm^2$ , which is indicative that phenomena observed above this threshold are not dependent on the ECSA, otherwise they would occur at lower current for sample *sPPS:PBI-OO*. Subtracting the kinetic component of the low frequency resistance allows to isolate the mass transport contributions,  $\eta_{MT}$ . Since  $\eta_{MT}$  is found to be mostly linear, it is possible to extrapolate its slope and obtain an area-specific resistance,  $ASR_{MT}$ . Results from this analysis are reported as a bar chart in Figure 5.42. It can be seen that conditioning increases the difference in  $ASR_{MT}$  between the two samples, but already at BoL mass transport limitations within *sPPS:PBI-OO* are more than 50 % higher than *sPPS:PBI-OO with ILs*. To be quantitative, the additional mass transport arising from exposure of the cathode catalyst to the hydrocarbon membrane amounts to  $24 \pm 3 m\Omega cm^2$  before conditioning and increases to  $48.0 \pm 1.6 m\Omega cm^2$  after.



Figure 5.42: Bar chart comparison of the extrapolated  $ASR_{MT}$  values before and after conditioning for *sPPS:PBI-OO* (without ILs) and *sPPS:PBI-OO* with ILs. The reduction  $ASR_{MT}$  possible through the addition of Nafion<sup>TM</sup> interlayers between the membrane and each electrode is reported with a line.

### 5.5.5 Limiting current

Subsequently, limiting current measurements were performed in an effort to acquire sufficient information to discriminate mass transport limitations between intermolecular gas diffusion (pressure dependent) to Knudsen or heterogeneous phase diffusion within ionomer-water layers (pressure independent). The study described in Section 3.3.4 and the obtained  $i_{lim}$  are used to calculate the respective values of  $R_T$ , which are plotted in Figure 5.43. Unfortunately, it was not possible to obtain data from *sPPS:PBI-OO with ILs* before conditioning. Several remarks are possible already from this unrefined overview. Firstly,



Figure 5.43:  $R_T$  measured at  $\chi_{O_2}^{wet} = 0.04$  at different pressures and conditions with the described samples.

measurements at 80 °C and 80 % *RH* (then called *Warm* conditions), shown as squares, exhibit a much lower transport resistance than the ones collected at 40 °C and 100 % *RH* (renamed *Cold* conditions). This is due to the expected soaking of the fuel cell in such conditions, therefore the path of oxygen to the catalyst will include diffusion through a liquid phase.

Secondly, the difference between *sPPS:PBI-OO with ILs* and *sPPS:PBI-OO* in drier conditions seems to be less relevant than in the soaked state. Lastly, for *sPPS:PBI-OO* conditioning leads to a small reduction in  $R_T$  at 80 °C and 80 % *RH* but is correlated to a much greater increase of the same at 40 °C and 100 % *RH*. For a more detailed comparison, results of the linear interpolation of  $R_T$  are listed in Table 5.8.

		Sample			% increase due to:		
		no ILs - BoL	no ILs - EoT	with ILs - EoT	ILs absence	conditioning	
Cold	$R_{NP} [{ m s}{ m cm}^{-1}]$	1.63 (0.02)	1.99 (0.02)	0.919 (0.007)	116 (3)	22 (2)	
	$R_P [ m s  cm^{-1}  bar^{-1}]$	0.980 (0.01)	1.062 (0.010)	0.534 (0.003)	99 (2)	8.3 (1.5)	
Hot	$R_{NP} [{ m s}{ m cm}^{-1}]$	0.507 (0.006)	0.491 (0.009)	0.289 (0.003)	70 (3)	-3 (2)	
	$R_P$ [s cm <sup>-1</sup> bar <sup>-1</sup> ]	0.300 (0.003)	0.292 (0.004)	0.265 (0.001)	10.1 (1.6)	-2.5 (1.6)	
% Reduction Cold-Hot	$R_{NP}$	69 (0.6)	75 (0.5)	68.5 (0.4)	9.8 (1.0)	9.1 (1.2)	
	$R_P$	69.4 (1.5)	72 (0.5)	50.2 (0.3)	44.7 (1.4)	4.4 (0.8)	

Table 5.8: Results of linear interpolation of  $R_T$  measurements at different pressures. Values reported are the average between repetitions at  $\chi_{O_2}^{wet} = 0.04$  and  $\chi_{O_2}^{wet} = 0.01$ .
It is pragmatical to begin the discussion of these results from the comment of  $R_P$  since it encloses information of intermolecular gas transport within the flow field, GDL and catalyst. Therefore, allowing to identify the presence of soaking, independently from any chemical contamination of degradation. In this respect, it is noticed that in *Cold* conditions, all samples experience a steep increase in  $R_P$ , despite their similarity during *Hot* measurements. This behavior could be interpreted as sensitivity to humidification state and is represented as the percentual reduction of a paramter from *Cold* to *Hot* conditions and is expressed in the rows reporting the % *Reduction Cold-Hot*. This phenomenon is  $31 \pm 1$  % more marked for *sPPS:PBI-OO*. This suggests that presence of interlayers is correlated with reduced soaking of the bigger porosities, where intermolecular gas diffusion takes place. For this sample, it is noticed that conditioning has a negative influence on  $R_P$  in *Cold* conditions, causing an 8.3 ± 1.5 % increase, while for measurements at *Hot* settings a slight decrease is registered  $(2.5 \pm 1.6 \%)$ . It seems that soaking behavior in *sPPS:PBI-OO* is made more subsceptible to relative humidity by conditioning. This could be explaned by the diffusion of sPPS within the catalyst, which being more subsceptible than Nafion<sup>™</sup> to humidity variations, could strengthen this correlation. Nevertheless the increased sensitivity can be quantified in a 4.4  $\pm$  0.8 % increase of  $R_P$  across conditioning.

Regarding  $R_{NP}$ , *sPPS:PBI-OO* shows higher mass transport limitations that *sPPS:PBI-OO with ILs* at all test conditions. This is indicative that even without soaking, the absence of interlayers is correlated with additional resistance to oxygen diffusion. In particular, at *Hot* conditions there is alredy a 70 ± 3 % increase in  $R_{NP}$ . As expected, this difference increases at *Cold* conditions to 116 ± 3 %. In relative terms, the evolution of  $R_{NP}$  due to different environment conditions is higher between samples than for  $R_P$ . This difference is quantified as an increased relative subsceptibility due to interlayers absence of 9.8 ± 1.0% against 44.7 ± 1.4 %, for  $R_P$  and  $R_{NP}$  respectively. This is mainly due to the fact that *sPPS:PBI-OO with ILs* has more even  $R_P$  values in the two tested conditions than  $R_{NP}$ .

Ultimately, this can be interpreted as a stronger tendence *sPPS:PBI-OO* towards soaking intermolecular gas diffusion paths. Nevertheless, sample *sPPS:PBI-OO* shows variation in sensitivity to relative humidity across conditioning of  $R_{NP}$ , quantifiable in 9.1±1.2%, a value higher than the one extracted for  $ASR_p$ . Therefore, conditioning procedure turn out to be more impactful on the pressure-independent term than on the pressure-dependent one. Since diffusion of oxy-

#### 5.5. DIFFERENTIAL CELL TESTING

gen is supposed to be halted by presence of wet layers and contaminants, it is attempted to discriminate these two effects.

Such an effort is proposed to be undertaken by considering the different nature of the transport resistances contributions merged into  $R_P$  and  $R_{NP}$ .  $ASR_p$  represents the additional obstacle due to soaking of gas diffusional paths, while  $R_{NP}$  also is affected by ionomer layers covering the electrodes. Therefore, the relative increase of  $R_P$  parameter associated to the absence of interlayer can be used to offset for this phenomena and obtain an expected  $R_{NP,exp}$  if no contamination of the catalyst was present. It is important to remind that due to the different morphology of the pores in which intermolecular gas diffusion and Knudsen diffusion takes place, also their capillary behavior will differ. Reason why a direct transposition is eventually not strictly correct. Nevertheless, by limiting this considerations to measurements performed in *Hot* conditions, it is possible to mitigate the influence of fuel cell soaking. In this way it is possible to assume that the difference between measured  $R_{NP}$  and expected  $R_{NP,exp}$  as an extra resistance, named  $R_{NP,extra}$  in Table 5.9.

		BoL	ЕоТ
$R_{NP}$ no ILs	$[s cm^{-1}]$	0,507 (0,006)	0,491 (0,009)
$R_{NP}$ with ILs	$[s cm^{-1}]$	0,289 (0,003)	
% diff $R_P$		13,2	10,1
$R_{NP,exp}$	$[s cm^{-1}]$	0,327 (0,003)	0,318 (0,003)
R <sub>NP,extra</sub>	$[s cm^{-1}]$	0,180 (0,007)	0,173 (0,010)
$\% R_{NP,extra}$		55 (2)	54 (3)

Table 5.9: Calculations to extrapolate the effect of contamination through the analysis of  $R_{NP}$  and  $ASR_p$  obtained from CCMs with and without Nafion @ demark interlayers between sPPS:PBI-OO membrane and electrodes.

It is obtained, through a rough estimation, that  $R_{NP,extra}$  due to catalyst layer contamination amounts to  $55 \pm 2$  % of the value obtained when no poisoning was visible. Also, this parameter seem to return the same value before and after conditioning, from which it is obtained a weighted average of  $R_{NP,extra} =$  $0.177 \pm 0.006 \ s \ cm^{-1}$ . It's invariance across test suggests that the cathode is essentially stable and it must have reached its equilibrium during the preliminal polarization curves.

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# Discussion of hypothesis for performance decay

Three hypothesis were formulated to explain the observed low performance and decay during conditioning of CCMs with sPPS:PBI-OO membranes:

- 1. Lack of mechanical adhesion could arise during testing;
- 2. During cathode starvation conditioning, an increased production of hydroxyl radicals could take place, leading to decomposition of the membrane;
- 3. Leaching of contaminants species from within membranes into catalyst layers.

By successive exclusions it was eventually possible to discard all alternatives but the last one, which has also been confirmed either by measurements reported in this thesis and ex-situ experiments carried out at Max-Planck-Institute that will be introduced in this chapter.

#### 6.1 DEGRADATION OF MECHANICAL ADHESION

Degradation of mechanical adhesion was appointed as a first hypothesis to explain performance loss. However, many fuel cell studies and applications are performed through the use of GDE, which consist in covering with electrocatalyst material the microporous layer. As a result, GDE approach doesn't ensure

#### 6.1. DEGRADATION OF MECHANICAL ADHESION

any mechanical adhesion between catalyst layer and membrane before testing. Therefore, mechanical contact has already been found to not be necessary for good performance. Nevertheless, good mechanical adhesion of catalyst layers onto sPPS:PBI-OO membranes was verified through peeling tests and SEM micrographs collected from cryo-breakages of CCMs described in Section 5.4.7. Peeling tests consisted in wrapping a CCM with duct tape on both sides and then trying to peel off the catalyst layer from the membrane by removing the tape. Before peeling, the sample was heated at 130 °C for 4 minutes to strengthen the bonding between tape and catalyst layer. The results of this simple testing can be seen in the pictures within Figure 6.1. These pictures show that after



Figure 6.1: Results on the peeling test of (a) *sPPS:PBI-OO* within the active area after testing and (b) *sPPS:PBI-OO* with *ILs* outside the active area.

testing it is not possible to remove relevant quantities of the catalyst layers from sPPS:PBI-OO membranes. On the contrary, this CCM displays embrittlement which leads to the membrane breaking while peeling the second electrode. However, before testing it is possible to remove almost completely this layer from a CCM prepared using interlayers. Since already at begin of life the performance exhibited by the sample with interlayers is decisively superior to the one without, mechanical adhesion cannot motivate the observed performance disparity. Furthermore, since cohesion between layers is proven after testing for *sPPS:PBI-OO*, also performance degradation is uncorrelated to mechanical adhesion of the catalyst layer to the membrane.

#### 6.2 Membrane decomposition due to radical attack

During conditioning, cathode air flow is interrupted for 45 seconds, as reported in 6.2.



Figure 6.2: Overlapped conditioning (or *break-in*) cycles with line opacity increasing with cycle number.

Within this period, the fuel cell passes from having a relevant potential to an abrupt drop associated with oxygen depauperation and equilibration of the electrodes. However, at all stages current is not zero. This implies that in the nearly 25 seconds in which cell potential is 0 V, HER will take place, causing the reduction of dissolved protons and hydrogen release. In this scenario, any oxygen residuals might spontaneously react with the produced H<sub>2</sub> forming a mixture of water and hydrogen peroxide. Given that  $H_2O_2$  decays into OH. hydroxyl radicals, an extremely oxidative environment could be expected. Indeed such conditions are considered to be ideal for cleaning Pt surface from organic production byproducts leading to catalyst activation. If this was the reason, we could even consider that Nafion<sup>™</sup> is not affected by it and might act as a chemical barrier since CCMs prepared with it as an interlayer do not display any decay during conditioning. However, a similar decay appears in the sample prepared with Nafion<sup>™</sup> only at the cathode, displaying the simmetry of such degradation which cannot be explained by a production of detrimental radicals at the cathode. Furthermore, chemical degradation could lead to abrupt performance loss only if taking place on a magnitude sufficient to disrupt ionic conduction, which would most likely be observable though SEM micrographs as inhomogeneities within the membrane. Although, this has not been observed and therefore this hypothesis can be discarded.

#### 6.3 LEACHING OF CONTAMINANT SPECIES

A possible explanation to performance losses occurring on both sides could be found in release from the membrane of contaminants. Small, water-soluble molecules might be transported as a side effect of water transport. Indeed, during the operation of a fuel cell, water is transported between the electrodes by electro-osmotic drag and back-diffusion, respectively taking place from anode to cathode and viceversa. Especially in the conditioning step, water transport from within the membrane is inverted twice at every cycle. During high current density operation the high electro-osmotic drag leads to principally water transport towards the cathode, while during air starvation the current is dropped. Therefore, water gradient originally generated by electro-osmotic drag is not anymore sustained and back-diffusion to the anode plays a major role in water transport.

Nevertheless, also within this hypothesis Nafion<sup>™</sup> could be considered to act as a buffer layer, stopping leached contaminants and preventing them from reaching the catalyst. These considerations allow to successfully explain two observations made from studying the dependence of conditioning behavior on the placement of interlayers (Sections 5.4.2 and 5.4.3). First, decay rate during conditioning is substantially proportional to the number or electrodes which are not protected by a Nafion<sup>™</sup> interlayer. Secondly, decay rate and galvanostatic impedance confirm that a CCM with only an interlayer at the cathode exhibits a slightly more relevant decay of the anodic performance than the counterpart without both interlayers. This could be due to the fact that a single Nafion<sup>™</sup> interlayer might act as an impenetrable wall for the diffusion allowing relaxation of the concentration gradient of contaminants to take place only at the anode side. Furthermore, observed electrochemical behavior of the cathode catalyst strongly suggest presence of unusual redox systems which might motivate the low ECSA available for hydrogen deposition and desorption. To exclude presence of amine salts leftover species which might act as contaminants and are employed in the manufacturing of membranes for their neutralization, Annette

Fuchs (MPI) performed potentiometric evaluation of chlorine. These measurements allowed to discard this possibility since the found concentration was 6 ppm, insufficient to motivate the observed catalyst poisoning. Followingly, it was hypothesized that sPPS itself might be the contaminant due to its high molecular mobility and polarity. Based on the missing ECSA, it is possible to estimate the amount of sPPS that should have leaked if every sulfonate group could adhere to a platinum nanoparticle poisoning an area corresponding to the monolayer density of  $H_{UPD}$ , which represents certainly an overestimation due to the bulkyness of  $-SO_3$ . However, this last assumption is also made to compensate the overestimation of poisoning efficiency, since it is considered that all the sulfonate groups will eventually poison a Pt site. Detailed calculations are reported in Appendix D. This estimation results in an area-specific leaching of 0.05  $mg_{sPPS} \ cm^{-2}$ . Considering a density  $\rho_{sPPS} = 1.6 \ g \ cm^{-3}$  for sPPS, leads to a membrane thinning of 0.31  $\mu m$ . This amount constitutes less than 10% of the sPPS employed. This low value is still consistent with the observation of no significant thinning for the membrane without interlayer's protection. Nevertheless, it was possible to directly observe localized formation of defects (Fig 5.34) and recognize the accumulation of polymeric material with subsequent disruption of the usual microstructure of the catalyst. Still, this situation occurs sparsely on the sample, therefore further evidence is brought to motivate the leaching hypothesis.

As a confirmation of these findings and to exclude further unconsidered alternatives, *ex-situ* experiments performed at MPI by Andreas Münchinger to quantify sPPS leaching are reported in Figure 6.3. Leaching is the only explanation for such measurement since the other process that could explain a loss of IEC, hydrolitic desulfonation, has been excluded by studies published as part of PSUMEA-3 project.<sup>[42]</sup> It is noticeable that decay seems to dramatically increase for blends made with sPPS possessing a lower EW. Since the version used within this thesis is composed of S-240, the expected leaching is somewhat midway between S-220 and S-260 displayed in the graph. Considering that to explain the performance loss observed, a leaching as low as 10% is sufficient, it becomes clear that the time scale to achieve it is much lower than the one recorder in this last figure.

#### 6.3. LEACHING OF CONTAMINANT SPECIES



Figure 6.3: Decay of IEC experienced by different sPPS:PBI-OO blends as a function of immersion time in distilled water at 80 °C. The number following the capital S in the legend stands for the EW of used sPPS, which depends on the sulfonation degree of the PPS backbone. Measurements have been performed at MPI by Andreas Münchinger within the project PSUMEA-3 funded by BMBF. Reprinted with permission of the author.

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# Conclusions and Outlook

In this thesis, a reliable and effective processing route is discussed for the preparation of fuel cells based on hydrocarbon membranes exclusively employing high-throughput techniques. At first, experiments were executed to improve the performance of a fuel cell based on sPPS:PBI-OO membrane with additional interlayers on both electrodes. It was possible to achieve a 22 % increase in power output in Standard conditions at BoL by reducing interlayer thickness from  $1.58 \pm 0.16 \ \mu m$  to  $1.05 \pm 0.13 \ \mu m$  while adopting a smoother and softer substrate for this layer. Smoothness of the substrate allows to coat evenly with extremely thin blade gaps, while the softness is speculated to reduce lamination pressure. Through SEM pictures it is observed that proposed process modifications lead to increased roughness of the catalyst-Nafion<sup>™</sup> interface and through *in-situ* cathode-CV it was possible to recognizer an increase in ECSA of 22.56  $m^2 g_{Pt}^{-1}$ corresponding to 45 % increase in catalyst utilization efficiency. Afterwards, a process for preparation of CCMs by direct decal transfer of PFSA-based catalyst layers onto hydrocarbon membrane was developed. In particular, it is found that varying the hydration state of ionomers without glass transitions allows to achieve sufficient softening to enable decal transfer in roll-to-roll processing.

The polymeric electrolyte used exhibited an encouragingly low ionic resistance, achieving  $ASR_{ion} = 24.8 \ m\Omega \ cm^2$  in Standard conditions, 80 °C, 100 % *RH* with a current density of 2.5  $A \ cm^{-2}$ . However, employed membranes exhibited a relevant increase of  $ASR_{ion}$  under dry conditions at low current densities, when ionic resistance reached 340  $m\Omega \ cm^2$ , registering more

than 13-fold increase compared to the best value.

More importantly, compatibility issues of a specific hydrocarbon ionomer, sPPS, are discovered and investigated through the preparation of fuel cells with Nafion® interlayers between membrane and electrodes. Performed experiments allowed to determine the cause of incompatibility in the leaching of sPPS from within the membrane. Relative results are discussed in Sections 5.4 and 5.5. In samples without any Nafion® interlayer, a lack of ECSA is identified since the first operation of the fuel cell. Furthermore, a common cathode starvation conditioning procedure was found to have a detrimental effect on the activity of both electrodes. During conditioning, performance degradation was found to be roughly proportional to the number of electrodes directly exposed to sPPS:PBI-OO membrane. An important point further developed in the end of this paragraph, consist in the stabilizing effect of Nafion® interlayer observed in fuel cells. The symmetry of decay during conditioning allowed to preliminarly argue that the cause could not reside in chemical degradation of the compounds employed in the membrane, since chemical degradation mechanisms proposed could only take place at the cathode side. Through SEM micrographs, it was possible to determine that no significant thinning of the membrane takes place with and without Nafion<sup>®</sup> interlayer as a consequence of testing. This finding allowed to strongly reject the chemical decomposition as a possible explanation for the performance difference between displayed samples. However, collected ATR-FTIR spectroscopies allowed to highlight a more relevant exposure of the reinforcement layer on the anode side than on the cathode. Observation of apparently discording results from these two *ex-situ* techniques is actually in accordance with the hypothesis of leaching from the membrane. Firstly, CCMs with Nafion® interlayers do not exhibit any contamination or performance degradation during conditioning. Indeed, based on the different water transport properties and nanomorphology of PFSA ionomers compared to sPPS, each Nafion® layer can be considered as a barrier preventing catalyst contamination. Considering this to be true, soluble species should be accumulated at the membrane-nation interface during testing. Subsequently, while cleaning off the catalysts in preparation of ATR-FTIR spectroscopy, it is possible that also these soluble compounds get washed out. This scenario is therefore consistent with experimental results and the proposed leading hypothesis. Moreover, it was possible to provide a rough estimation of membrane thinning that would

justify the observed catalyst contamination, 0.31  $\mu m$  which is not detectable due to surfacial roughness of electrodes and membrane thickness deviation. Unfortunately, presence of sPPS within removed catalysts was not investigated and remains a possible research topic for more systematically determining the species responsible for contamination.

A quantitative evaluation over the effect of leaching was attempted by estimating the increase in mass transport resistance observed resulting from the preparation of fuel cells without interlayers. The parameter that was found to embody the largest share of performance difference due to contamination was  $ASR_{LFR}$ , from which it was possible to isolate a constant mass transport resistance ( $ASR_{MT}$ ) arising at currents above 1  $A cm^2$ . The absence of interlayer was correlated with an increase in  $ASR_{MT}$  amounting to  $24 \pm 3 \ m\Omega \ cm^2$  before conditioning and increases to  $48.0 \pm 1.6 \ m\Omega \ cm^2$  after said procedure. Limiting current measurements allowed to assess the intermolecular gas diffusion independently from Knudsen and heterogeneous phase diffusion in order to discriminate limitations arising due to water soaking and oxygen permeation through contaminants independently. Especially, it was found that  $R_{NP}$  is not affected by conditioning and a portion of the measure is not explainable in terms of soaking but rather in terms of limited gas diffusion through sPPS covering catalyst particles. This term was quantified in terms of  $R_{NP,extra} = 0.177 \ s \ cm^{-1}$ and equals to 55 % of the  $R_{NP}$  obtained from a sample possessing interlayers to separate electrodes and membrane. This additional gas diffusion obstacle was found to be constant across conditioning, allowing to understande that a stable condition of contamination is achieved at the cathode catalyst layer during the preliminar polarization curves. Furthermore, limiting current measurements allowed to highlight that especially at 100 % RH, the direct contact between hydrocarbon membrane and catalyst layer leads to extensive soaking which involves also the MPL and GDL. Nevertheless, also this problem can be mitigated with the addition of a perfluorinated interlayer.

Additionally, it is argumented that satisfying performance were measured from a fuel cell based on sPPS:PBI-OO membrane with the addition of Nafion® layers to separate polymer electrolyte and electrodes. Initially, such interlayers were implemented to enable the preparation of CCMs, but along this study their role was discovered to be much more faceted. Specifically, as little as 1  $\mu m$  of Nafion® is sufficient to halt sPPS from leaching and poisoning the catalyst as

well as preserving water management capabilities of perfluorinated electrodes. This double role allowed to register a maximum power density of 2.46  $W cm^{-2}$ while testing with  $H_2/O_2$  using a differential configuration. Actually, the power measured was limited by the current density achievable by the testing rig setup and it is possible that a higher power output could be achieved by increasing further the circulating current. These additional layers displayed a remarkably low ionic resistance  $ASR_{i,IL} = 0.38 \pm 0.09 \ m\Omega \ cm^2$ . However, their thickness plays a crucial role and an increase of just on 1  $\mu m$  leads to a reduction of maximum power output by 22 % at 2.5  $A cm^{-2}$  in a serpentine cell setup tested at *Standard* conditions. Nafion<sup>™</sup> layers are enabled to assolve these functions by their phase-separated nanomorphology which inhibits excessive hydration and constitutes a blocking layer for the passage of bulky sPPS-240 polymeric chains that on the other hand become mobilized under high relative humidity and temperature. The usage of ionic cross-linking between sPPS and PBI-OO does not produce the desired effect of immobilizing the polymeric strands, possibly due to the fading of such interaction in the described environment. Nevertheless, studied membranes achieved high performance in terms of ionic conductivity and displayed to be employable in an high-throughput process.

As concluding remarks I would like to outlook at the perspectives opened by this study. Firstly, it can be speculated that research in the field of hydrocarbon ionomers should take into account the role played by the interlayers prepared in this study and aim to develop ionomers with more stable hydration across the scale of relative humidities and temperatures required for HT-PEMFCs, of utmost important is to avoid leaching of poisoning species into the catalyst layer. Secondly and lastly, identifying the mechanism of poisoning and the species involved might lead to define mitigation strategies that eventually would enable a higher degree of freedom in the choice of polymer electrolytes.

# Appendices



# Conversion of line pressure into conventional pressure

During lamination, the total force applied between the rolls is registered. Then it is displayed to the operator as a line pressure, followingly renamed line-load *LL* expressed in  $N mm^{-1}$ , after normalization of the total force by the width w of the sample. This is due to the fact that there is no direct way of measuring the contact area between laminated sheets and calendering rolls. However, an estimation of this is possible by assuming solely an elastic compression of laminated sheets. Firstly, it is considered that only a small part of the rolls is in contact with the laminated sheets since the compression,  $\Delta z$  is always below 100  $\mu m$  and the radius of them is r = 50 cm. Therefore the arc of circumference being involved in the contact can be assumed to be reasonably small to operate the approximation  $\sin x \approx x$ . Furthermore, from geometrical considerations it is possible to obtain the arc angle ( $\theta$ ) considering the cosine of the arc angle.

$$\cos\theta = 1 - \frac{\Delta z}{2r} \tag{A.1}$$

But also that a second order Taylor expansion of the cosine is:

$$\cos\theta = 1 - \frac{\theta^2}{2} \tag{A.2}$$

This way the arc angle is obtained as  $\theta^2 = \Delta z/r$ . Since  $\sin \theta \approx \theta$ , the projected contact length is given by:

$$l = 2r\sin\theta = 2\sqrt{r\Delta z} \tag{A.3}$$

Now, the total contact area of the rolls with the laminated sheets can be calculated simply as:

$$Area = l \times w \tag{A.4}$$

And the average pressure  $P_{avg}$  applied to the sample as:

$$P_{avg} = \frac{LL}{l} = \frac{LL}{2\sqrt{r\Delta z}} \tag{A.5}$$

As a guide for the reported cases, when the compression is 100  $\mu m$  and the measured line pressure is 200  $N mm^{-1}$ , the average pressure applied to the lamination assembly is estimated to be 141 *bar*.



#### **B.1** Recovery from Hot & Dry conditions

On the differential setup, it is possible to by-pass humidifaction of the inlet gases. Therefore, measurements in HD conditions are performed with completely dry flows. Due to dryness, the interaction between sulfate superacid groups and Pt nanoparticles is not shielded by water molecules and adsorption may occur. In order to redissolve the sulfate functions, a recovery is enacted. The procedure requires step-wise approach of very low potentials in cold and wet condition. In particular, temperature and relative humidity are set respectively to 40 °C and 100 % *RH*. Stoichiometry of flows is set to  $\lambda_{an} = 2$  and  $\lambda_{cat} = 5$  with H<sub>2</sub>/Air atmospheres at 1 *bar*. As can be seen in Figure B.1, cell is controlled potentiostatically to operate step-wise potential reduction until reaching 0.05 *V* when it is held for 20 minutes. The main aim is to sustain abundant water formation for long enough to establish once again the Pt surface and sulfate freedom. Afterwords, potential is risen once again to 0.9 *V* when the control is switched to galvanostatic in order to head into the following procedures witholding OCV.

#### B.1.1 AST1

AST1 allows to emulate the aging associated with power output variations, especially in a fuel cell for automotive applications. To adjust power output to the instant requirement, the load (output potential, V) of a fuel cell must be

#### B.1. RECOVERY FROM HOT & DRY CONDITIONS



Figure B.1: Potentiostatic control for sulfate dissolution after testing in HD conditions for differential cell testing.

changed. Since the anode is a nearly unpolarizable electrode, only the cathodic potential is considered to be affected by these variations. In the usual operation of a fuel cell, the potential is varied in a region which includes platinum oxidation and reduction reaction, as shown in the plotted CV (see Fig.3.6). For this reason, AST1 consist in a square wave potential with a lower limit of 0.6 *V* and an upper limit of 0.95 *V* and a holding time of 1 *s* for each step. Temperature and relative humidity are identical to standard conditions (80 °C and 100 % *RH*), but gases are H<sub>2</sub>/N<sub>2</sub> respectively at anode and cathode, with gas flows of  $Q_{an} = 0.2 Nl/min$  and  $Q_{cat} = 0.8 Nl/min$ . The 30 thousand cycles are only interrupted to record cyclic voltammograms at intermediate points of the procedure.

#### B.1.2 AST2

Another important phenomena occurring within an operating device is corrosion due to the oxidation of carbon support at the cathode electrode, subsequent wash-out of the water soluble byproducts but more importantly detachment of catalyst nanoparticles from the support. To replicate this phenomena in an accelerated manner, AST2 has been developed. During this procedure, temperature, gases, flows and relative humidity are set to the same values as for AST1. Radically different is the potentiostatic control operated in this step. Potential is controlled in a triangular wave between 1 V and 1.5 V with a scan

rate of  $0.5 V s^{-1}$  for 500 cycles with a stop after 250 cycles to perform a CV in order to monitor loss of ECSA.

#### B.1.3 Recovery from AST2

Before characterizing the performance at EoT, the cathode catalyst undergoes a recovery procedure which is meant to ripristinate the electroactive surface area. This goal is pursued by bringing the conditions of the cell to  $80 \,^{\circ}C$ ,  $100 \,^{\circ}RH$ , with  $1 \,NL \,min \,H_2$  flow at the anode and  $2.5 \,Nl \,min$  air flow at the cathode while holding the potential at  $0.3 \,V$ .



### Indentation depth measurement

To measure the indentation of catalyst layer into the Nafion<sup>TM</sup> interlayer, cross section of cryo-breakaged CCMs were observed by FE-SEM. Then, via an image analysis software, ImageJ<sup>[43]</sup>, was used to apply the macro *InteredgeDistance*  $v.14^{[44]}$  shared on Image.sc Forum.<sup>[45]</sup> This short program allows to select two separated collections of points to be interpolated by splines and measure the distance between these lines in 15 distinct points. Then the program returns average, standard deviation, minimum and maximum value.



Figure C.1: FE-SEM micrograph showing the convolution lines of the protrusion and valley profiles. Also the segments used to measure the indentation depth are represented in between the two profiles.



### sPPS poisoning estimations

The observed result of catalyst poisoning is a reduction in ECSA from  $\approx 45 \ m^2 g_{Pt}^{-1}$  to  $\approx 17 \ m^2 g_{Pt}^{-1}$ . The cathode catalyst layer exhibiting such reduced ECSA has a platinum loading of 0.45  $mg_{Pt} cm_{MEA}^{-2}$ . It is more straightforward to discuss this effect in terms of roughness factor, *r f*, which expresses the available catalyst surface area per unit geometric area of the device. Therefore, *r f* is calculated by the ratio between ECSA and platinum loading, to obtain an adimensional value that for the sake of clarity can be accompanied by a fictious dimensional unit of  $[cm_{Pt}^2 cm_{MEA}^{-2}]$ . Unpoisoned samples exhibit usually a roughness factor  $r f_{unpois.} \approx 200 \ cm_{Pt}^2 \ cm_{MEA}^{-2}$ , while the poisoned samples had a value  $r f_{pois.} \approx 75 \ cm_{Pt}^2 \ cm_{MEA}^{-2}$ . Therefore, the missing roughness can be obtained from the difference of these two values and estimated to be  $\Delta r f \approx 125 \ cm_{Pt}^2 \ cm_{MEA}^{-2}$ . Considering a monolayer density of  $\rho_{ML} = 1 \times 10^{15}$  monomers  $cm_{Pt}^{-2}$ , the amount of contaminant that should have leached from the membrane per square centimeter of the device is  $n_{leach} = \Delta r f \times \rho_{ML} = 1.25^{17} monomers cm_{MEA}^{-2}$ , or  $n_{leach} = 2.08 \ mol \ cm_{MEA}^{-2}$ . If it is considered that every leached monomeric unit ( $M_M = 240g/mol$ ) is effectively a poisoning species, the amount of polymer per unit area of the device necessary to explain this degree of contamination is  $m_{leach} = 0.05 \ mg_{sPPS} \ cm_{MEA}^2$ . Given that the density of sPPS is  $\rho_{sPPS} \approx 1.6 \ g \ cm^{-3}$ , the resulting membrane thinning from this effect should be  $\Delta t = 0.31 \ \mu m$ .

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