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# Interplays between preparation and processing of the catalyst ink in the manufacturing of a proton exchange membrane fuel cell catalyst layer

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## Abstract

Catalyst inks are formulated for Catalyst Layer (CL) fabrication of Proton Exchange Membrane Fuel Cells (PEMFCs) electrodes. Despite the overall fabrication process being quite simple and numerous innovations on PEMFC components having emerged, there is to this day no state-of-the-art rationalization of formulating inks and fabricating CLs. This grey area comes from a lack of understanding on the links between properties, structures and performance within the CL fabrication process. This paper first reviews the preparation of catalyst inks, which are primarily composed of an ionomer, catalyst, solvent, and may sometimes include additives such as antioxidants. Recent advances in understanding the properties and interactions of these components are highlighted, emphasizing their influence on ink behaviour and processability. In a second section, the discussion turns to ink coating techniques, such as spraying and printing, and examines how these methods impact the structural, mechanical, and chemical characteristics of the resulting CL. Drying processes are also considered, with attention to how different approaches affect the final properties of the CL. By analysing the interplays between ink formulation, coating, and drying, this work sheds light on the feedback-driven, iterative dynamics that underpin CL fabrication in PEMFCs, aiming to guide more rational and effective design strategies.

## Keywords

PEMFC

Catalyst ink formulation

Catalyst layer fabrication

Structure-performance relationship

Fuel cell optimization

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# 1. Introduction

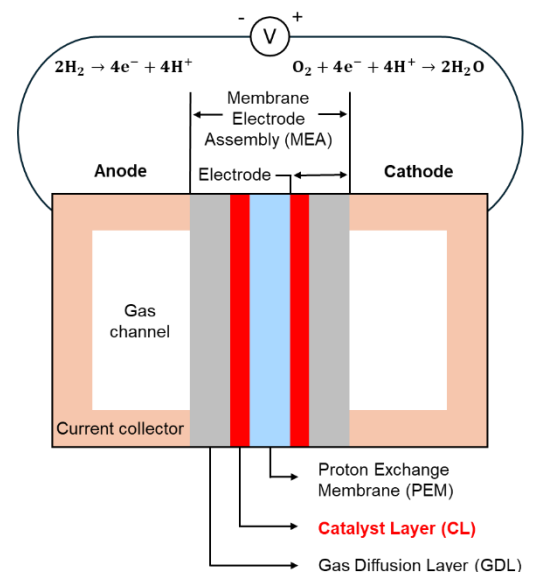
## 1.1. Broader context

As of common knowledge, there is an ever-growing demand for energy. Despite fossil fuels shortage and emerging new energy supplies and technologies, the demand for fossil fuels is expected to continue to rise significantly [1,2]. Among greenhouse gases sources, the transport industry is responsible for a significant part of the emissions [3,4]. Thus, the Proton Exchange Membrane Fuel Cell (PEMFC), seen as a promising technology to counterbalance the use of fossil fuels, has been paving the way for clean mobility for the past few decades, as a zero-emission electricity source [5–11]. In fact, thanks to their high power density and low operating temperature [5], PEMFCs hold a significant potential for many application domains, such as stationary and portable power generation systems or precisely the transport industry [10,12]. Furthermore, PEMFCs offer improved functioning over conventional liquid electrolyte fuel cells thanks to the ionomeric material in both the membrane and the catalyst layer, which enhances both performance and stability of the cell [13].

In an effort to improve PEMFCs performance and competitiveness, innovations on fuel cell components and fabrication processes have been made, whether it be on the proton conducting membrane [14–16], ionomer [17,18], gas diffusion layers [19], catalyst [20,21], or electrode fabrication process [22–26]. Thus, the cost of PEMFC production has consistently been plummeting over the past decade, promoting their accessibility [27]. However, lifetime and durability have not yet proven to be sufficient and electricity conversion yields are still to be improved in order for PEMFCs to thrive and reach commercialization competitiveness [6,28,29]. As of today, some aspects of PEMFC fabrication are still challenging. Platinum still accounts for half of the total production cost [30], and the sourcing or production of dihydrogen remains problematic for numerous reasons [31–34]. Moreover, there are still lacks in the comprehension of the interactions between the components and different constituting parts of the PEMFC [10,35], which hinders progress.

## 1.2. PEMFCs – brief overview and general principles

PEMFCs convert chemical energy into electrical energy through the redox reaction between gaseous  $H_2$  and  $O_2$ . The classical PEMFC is composed of several layers, as illustrated by **Figure 1**. The external layers of the cell are the anode and cathode, where both gases are distributed, and current is collected. In between those poles is the Membrane Electrode Assembly (MEA). The proton exchange membrane is at the heart of the cell, separating the two electrodes while allowing protons to travel. The electrodes are composed of a gas diffusion layer which evenly distributes fuel onto the catalyst layer outer surface. This catalyst layer is the active layer of the cell, where reactions between the fuel gases take place; it is also the focus of the review. This layer is prepared via a multi-step process, where a catalyst ink is first formulated, composed of the ionomer, catalyst and solvent, which then undergoes a dispersion step to result in a homogenous ink. This ink is coated onto either the membrane or the gas diffusion layer, and dried, to result in the porous catalyst layer [36].



**Figure 1:** Scheme of a single PEMFC

There are several references of theoretically ideal catalyst layers and MEA designs [37–39]. It is recommended for catalyst layers to provide high electrocatalytic activity for reactions, high electrochemical surface area and good electronic and ionic transport. Moreover, high porosity is preferable for efficient two-phase transport of gas and water, while small pore size is suggested to ensure high capillary pressure for efficient water transport. Finally, catalyst layers must provide chemical stability and durability towards contaminants [37]. As for the MEA design, recommendations underline the importance of interactions between the layers. MEAs should have a high active surface area, an optimum component distribution for maximal conductivity, uniform mechanical forces should apply across the entire surface to provide contact between the layers and minimize contact resistance, hydrophilicity should be controlled to ease water management. Finally, the MEA is to be designed to ensure mechanical integrity and stability of the overall cell over operating conditions [38]. All these specifications make catalyst layer design a multi-parameter challenge with potentially infinite combinations of components, formulation and processes.

### 1.3. Scope of this review

Many reviews can be found on the more practical implications of catalyst ink and catalyst layer preparation processes, that's to say on the optimization of industrial protocols in order to target desired fuel cell functioning through the use of novel materials and innovative methods [6–8,19,22,40–42]. Thus, the majority of research articles found on catalyst layers, and on PEMFCs in general, are performance-driven, highlighting the appeal of the topic for researchers and industries [13,43–52].

Yet, if efficient solutions to boost performance and durability are often found, grey areas remain, especially on the links between properties of catalyst ink components, structures present within the ink and the catalyst layer, and performance of the final fuel cell. As a result, there is no state-of-the-art rationalization of formulating catalyst inks and fabricating catalyst layers. For example, there is no consensus on which type of solvent to use for catalyst ink formulation. While some studies favour the use of high-boiling-point solvents to slow solvent evaporation and prevent the formation of defects [53], other works recommend the use of low-boiling-point solvents to facilitate the drying process [54].

This review aims at offering a comprehensive way of looking at the challenge of designing a catalyst layer for PEMFC electrodes in an attempt to bridge the gaps between properties, structures and performance and highlight the areas where challenges in electrode manufacturing persist. The catalyst layer fabrication process is hereby considered as a whole, underlining the fact that primary parameters such as ink components' physicochemical properties, have an impact on every step of the process, from formulation of the ink to operation of the catalyst layer.

## 2. Catalyst ink preparation process

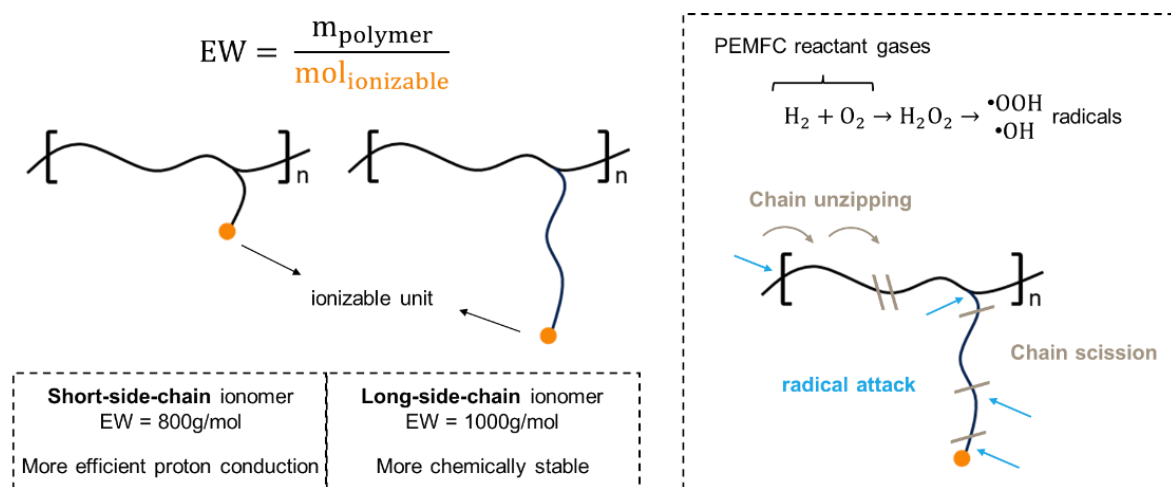
The first step in the fabrication of a catalyst layer for PEMFC MEA is the preparation of a catalyst ink. This step involves a mixture of three main components, namely an ionomer, a catalyst and a solvent, which undergo a dispersion process to obtain a homogeneous slurry. The extensive catalogue of choices for each of these components and dispersion methods, as well as the numerous experimental parameters such as ionomer to catalyst ratio, solid content, potential additives or energy inputs give rise to an ocean of formulation possibilities. The purpose of this chapter is to give some insight about the links between the ideal specifications of catalyst ink preparation, the intrinsic properties and interactions of the components, and the behaviour of the ink during dispersion in order to get a broad understanding of the implications that each parameter has on the overall preparation process, thus shedding light on the challenges to be tackled when designing a catalyst ink formulation methodology.

## 2.1. The main components - impact on ink properties

### 2.1.1. The ionomer

The early 2000's marked the beginning of the commercialization race for Perfluorosulfonic Acids (PFSA) in PEMFCs [55] which had slowly been replacing polytetrafluoroethylene (PTFE) both in membrane and in electrode preparation [5]. Their PTFE backbone offers high mechanical and chemical stability, their amphiphilic structure allows for a tuneable hydrophilicity of materials, and the ionizability of their side chains sulfonic acid end is of great interest for proton conduction in the MEA.

PFSA ionomers are differentiated by two main characteristics, namely the equivalent weight (EW) and the length of the side chain, as displayed by **Figure 2**. The equivalent weight is the mass of polymer per mole of charged sulfonic acid side chain. It plays a role in ionomer chemical stability and crystallinity and gives an indication on side chain occurrence rate alongside the backbone [56]. Side chain length helps categorize PFSA ionomers into two groups: Long Side Chain (LSC) and Short Side Chain (SSC).



**Figure 2:** General structure of ionomers, equivalent weight (EW) and typical degradation mechanisms

For their being the hypothetical ideal candidate for use in PEMFC electrode preparation, the physico-chemical properties of PFSA have been studied, whether it be as is or in solvent mixes [57–59], and patented molecules such as Nafion have progressively gained in popularity [57,60–62]. Nafion is a LSC PFSA ionomer developed by DuPont in the 1960s and has been consistently used as a reference PFSA ionomer in studies on PEMFCs ever since. Despite being the benchmark for PFSA, Nafion is, however, not the only ionomer used nowadays in PEMFCs, and an extensive field of research is dedicated to aiming towards the best suited candidate for high power high durability fuel cells. In particular, more and more SSC ionomers have emerged in recent years, like Aquivion, produced by Syensqo.

It has been established over the years that the ionomer side chain length and EW are dominant characteristics in determining ink and catalyst layer properties [17,63,64]. In a study on the impact of ionomer side chain length and equivalent weight on transport resistances in PEMFCs cathodes at high current density, Ramaswamy *et al.* [63] concluded that PFSA equivalent weight was directly linked to the performance of the resulting catalyst layer for it was responsible for tuning physico-chemical properties of the formulations in a way that impacts proton and dioxygen transport resistance in the catalyst layer. It was observed that a decrease in equivalent weight led to a lowering of transport resistances, hence better polarization performance at high current densities.

More precisely, a consensus tends to be reached on the advantage of SSC over LSC ionomers [11,18,24,65–68]. Several studies can be cited, among which Aquivion is consistently reported to lead

to PEMFCs providing higher ion exchange capacity, a more homogeneous ionomer proton conduction network and higher power densities compared to Nafion based PEMFCs. For example, both Ren *et al.* [67] and Li *et al.* [24] observed advantages for Aquivion over Nafion in terms of overall cell performances and macrostructures. In their study, Li *et al.* [24] observed that Aquivion based cells exhibited better performance at various current densities and higher output power under various operation temperatures. In parallel, Ren *et al.* [66] concluded that due to its higher ion exchange capacity, Aquivion formed a better proton conduction network within the catalyst layer. These findings are in concordance with the results reported by Malek *et al.* [65] in a study on the simulation of structural behaviour of Aquivion and Nafion in various dispersing solvents. It was in fact observed that Aquivion systems lead to higher diffusion coefficients for both water and hydronium ions, which is interpreted as the subsequent catalyst layer presenting less transport resistance thus higher power density.

However, in terms of intrinsic properties, the lead tends to be held by LSC PFSA ionomers. In fact, Aquivion is often reported to have weaker structural stability than Nafion [18,67,69]. In a study on the effect of ageing on structural stability of catalyst ink, Ren *et al.* [67] compared the physicochemical properties of Aquivion-based catalyst inks with those of Nafion-based catalyst inks before and after a short storage period of two days. On the one hand, Nafion based inks were able to recover their initial properties, such as particle size distribution and viscosity after redispersion. On the other hand, it was observed that Aquivion based inks exhibited a time-dependent adsorption behaviour of the ionomer onto the catalyst particles, especially during the storage period, which resulted in a decrease of chemically active sites availability, ink sedimentation and deteriorating of the overall network structure within the catalyst layer. Those phenomena were found to be irreversible. Along the same lines, Talukdar *et al.* [18] found that LSC based catalyst layers proved to be more reliable for long term application than SSC based catalyst layers for the ionomer being more chemically stable as a proton conduction network through operating conditions.

Overall, side chain length and ionomer equivalent weight are critical parameters regarding their impact on catalyst ink properties. At a molecular scale, as observed by Clark *et al.* [64], such differences could have to do with side chain flexibility. In fact, through computational methods, it was concluded that not only the side chain length but also the nature of the dispersing solvent had an impact on atomic bond rotations and rotational potential energy surfaces, especially near the sulfonic acid ends, thus impacting the ionomer conformation. The impact of the dispersing solvent on the structures and properties of catalyst inks is discussed in more details in the next part of this section.

Besides tuning catalyst ink properties, PFSA ionomers will also be prone to different degradation mechanisms, as seen on **Figure 2**. A majority of the studies on PFSA ionomer degradation focus on PFSA ionomer membranes [56,70–73], which are a more concentrated version of PFSA ionomer dispersions. Among those studies, a prevalence of end group driven degradation mechanisms is represented. The most common degradation of PFSA ionomer reported in the literature is the chemical condensation of sulfonic acid end groups [71,74,75]. Unzipping alongside the backbone may also be observed [46], but is more frequently reported in operating conditions of the fuel cell, due to the high likelihood of peroxide radical attack.

From a practical point of view, in terms of quantified parameters for catalyst ink preparation, there is no consensus about the optimal ionomer content for an ink. On average, there are two groups of ionomer contents reported in the literature. On the one hand, numerous studies prone a low-ionomer-content way of formulating inks, with ionomer content generally not exceeding 5 wt% [17,76,77], for there not only are solubility and sedimentation threshold issues arising above that concentration, but also mass transport deterioration due to the blockage of reaction sites when the ionomer

concentration is too high. On the other hand, certain studies argue that the more catalyst coverage by the ionomer the better the cell performance [78,79] because of the prevalence of proton conduction networks. In most cases however, the ionomer content needs to be optimized for every specific ink formulation process [25]. For example, Cho *et al.* [45] compared the impact of relative humidity on the performances of fuel cells based on inks with different ionomer contents. It was observed that optimum ionomer content needed for highest cell performance decreased with increasing relative humidity. This is explained by the fact that sufficient ionomer content is necessary to ensure cell hydration and operating environment.

Among the studies on fine tuning the ionomer structures and contents in order to optimize catalyst layer performances, further treatments and innovations on PFSA ionomers can be found. Shin *et al.* [14] observed that SSC structural stability could be modified and potentially improved through thermal annealing, by alteration of the ionomer crystallinity. Modification of the chemical structure of PFSA ionomers is also presented as a path to improve their proton conductivity. For example, in a study on chain extended ionomers, Su *et al.* [80] showed that proton dissociation of sulfonic acid with water could be controlled by adding a tuneable number of imide groups to the ionomer side chains. This is particularly useful when working at different levels of hydration since it was reported in another study [45] that the optimum ionomer content was dependent on the relative humidity of the cell environment. Along the same line, chemical modification of the ionomer backbone is explored. For example, highly oxygen-permeable ionomers have been shown to display better cell performance [81,82]. These ionomers present the incorporation of a three-dimensional rigid monomer into the backbone - typically a ring-structured monomer. These rigid monomers stiffen the hydrophobic matrix, which in turn resists chain packing, allowing better oxygen permeation at the ionomer/catalyst interface, thus improving the accessibility to reaction sites.

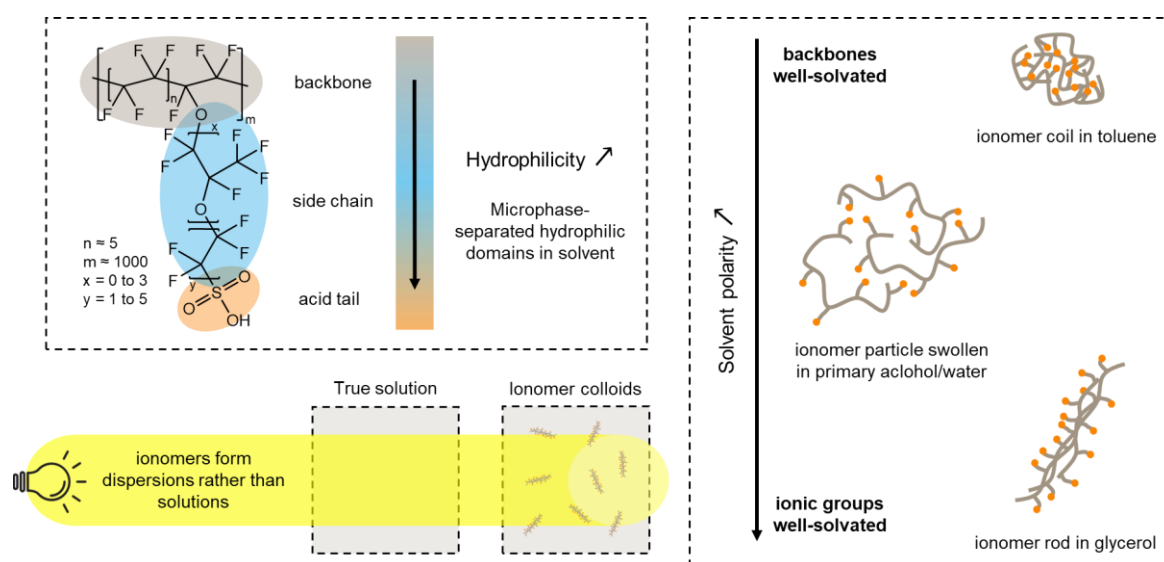
All in all, there are numerous parameters regarding the use of PFSA ionomers in catalyst ink preparation to be taken into account to ensure the best possible proton conduction potential without having to impair mechanical or chemical stability. Side chain length, EW, ionomer content and degradation all affect the performance of the final cell for they each play a role in forming the catalyst ink structure and properties. For now, there does not seem to be a universally preferable PFSA ionomer in the literature, and studies invariably report the uniqueness of each situation when formulating catalyst inks. Researchers however manage to find new ways of tailoring formulations for them to result in the best performing cells.

### 2.1.2. The solvent

There are a great number of solvent choices in the literature concerning the formulation of catalyst inks for PEMFCs. From water/alcohol mixtures to polyol blends, and even formulations with other organic solvents such as n-methyl-2-pyrrolidone or n-butyl acetate, the solvent choice in experimental studies is usually found to be determined case by case, and mostly in an empiric fashion, based on the materials, conditions and other targeted specificities of the studies [36,83–86]. As seen with the choice of ionomer, determination of the best-suited solvent for catalyst ink formulation for use in catalyst layer preparation in PEMFCs is not a “one size fits all” type of question, since variations in the materials and methods used along the catalyst layer fabrication process, such as ink dispersion method or ionomer/catalyst ratio, all tend to modify cell performance and induce a need to adapt the solvent [35,85,87].

Ionomers, and more particularly PFSA ionomers, are known to form dispersions rather than solutions when added to a solvent, as illustrated by **Figure 3**, with typical particle / aggregate sizes ranging from a few nanometers to several hundred [86]. Due to its amphiphilic nature, the ionomer demonstrates

different interactions with the dispersing agent depending on its polarity [84]. This results in a great variety of structures adopted by the ionomer and determined by the nature of the solvent [86,88,89], as shown on **Figure 3**. For example, in a study on the morphology of Nafion in various dispersing media, Welch *et al.* [86] observed three distinct types of structures: Nafion particles were found to form well-defined nanometric cylindrical rods in non-aqueous polyol medium such as glycerol or ethylene glycol, whereas they formed less-defined swollen particles once put in binary water/alcohol mixtures. These changes in ionomer structures and conformations are known to impact the ink physical properties such as viscosity. Ink viscosity was shown to be linked to ionomer structures within the ink at the molecular scale in a study on Nafion dispersions in water/ethanol mixtures by Gupit *et al.* [90]. It was observed through rheological measurements that the ink rheological behaviour was affected by the nanostructures of Nafion, which were linked to the water/ethanol ratio and Nafion concentration. More precisely, three different rheological regimes have been identified upon Nafion concentration variation in given water/ethanol ratios. At low ionomer concentrations, the systems behaved as dilute dispersions, progressively transitioning to semi-dilute unentangled and then entangled regimes as the concentration increased. Nafion particle structures were identified as consistently cylindrical, and the changes in dispersion viscosity were attributed to the complex microscale arrangement of Nafion and interparticle interactions. These entangled arrangements were found to be responsible for the shear thinning behaviour observed at higher Nafion concentrations.



**Figure 3:** PFSA ionomer chemical structure and solvent effects on aggregate morphology

One phenomena that is commonly described in studies on the impact of solvent composition on catalyst ink dispersion properties and ionomer structures is swelling, which is often reported to be driven by the alcohol content of the solvent mixture used as the ionomer dispersant [91,92]. Flory-Rehner theory describes swelling as the equilibrium state between the entropy of polymer chains and the enthalpy of mixing [93]. Interactions with a good solvent will induce a stretching of polymer chains, to a point where physical resistance to stretching will be encountered, resulting in a decrease in entropy, thus developing an elastic retractive force in the polymer network. This phenomena is experimentally observed through rheological viscoelasticity measurements, such as in the study on the structure and rheology of PFSA dispersions in water/alcohol by Khandavalli *et al.* [94]. Swelling of PFSA ionomer membranes has been thoroughly investigated since it dictates processability and stability [74,95–97]. Swelling also affects the accessibility of the ionomer sulfonic end groups, which will consequently impact the number of active sites within the ink [78,98,99]. A polyelectrolyte effect is reported in some studies for ionomers, especially for PFSA in polar solvents [90,100,101]. This

polyelectrolyte effect, as primarily described by Fuoss and Strauss [102], refers to the counterintuitive behaviour wherein the reduced viscosity—defined as the specific viscosity normalized by polymer concentration—increases as the solution is diluted. This contrasts with neutral polymer solutions, whose viscosity typically decreases with dilution. Ionomers are different from polyelectrolytes in the sense that their ionized side chains content usually does not exceed 15 mole percent, as opposed to 80 to 100 mole percent for polyelectrolytes [103]. Thus, the polyelectrolyte effect tends to be lesser in ionomer dispersions.

Interactions between ionomer and catalyst particles are also influenced by the nature of the dispersing agent [104–108], thus they are also to be taken into account when choosing the best-suited solvent for formulating the catalyst ink. The most common impairment resulting from the nature of the dispersion medium, in this case, is the excessive ionomer coverage of the surface areas that are electrochemically active, leading to a decrease in cell performance [104]. More specifically, the role of the solvent is here to ensure optimum contact between the ionomer and the catalyst to give the best ionomer coverage and catalyst distribution possible. This step is important for once the catalyst layer is formed, the resulting ionomer/catalyst network will not only have to ensure cell physical integrity but also provide adequate proton and gas conduction networks [109]. This aspect is discussed in further details in Section 3. Furthermore, different interactions between ionomer and catalyst also lead to different ink stability, as highlighted in the review by Hatzell *et al.* [110] and shown by *Taning et al.* [105] through the study of ink sedimentation dynamics. This study linked the solvent composition to the sedimentation dynamics of several catalyst inks through particle size analysis, rheological behaviour and ink stability considerations. It was found that for water/N-propanol mixtures, the water/alcohol ratio resulted in a change in ionomer/catalyst interface structure. More precisely, water-rich environments were found to favour the adsorption of ionomer onto catalyst particles thus a thicker ionomer coverage and larger aggregates, whereas alcohol-rich environments displayed a majority of free ionomers and weaker ionomer/catalyst interactions. Interestingly, contradictory conclusions were reached by Kumano *et al.* [111], who found that the amount of adsorbed ionomer was promoted by the presence of alcohol in the dispersion medium. These differences could be due to variations in the formulation parameters, and the lack of comprehensive conclusions underlines once again the acute sensitivity of catalyst ink properties to experimental conditions.

Overall, the solvent environment is of great influence on both the ionomer and ionomer/catalyst dispersion morphologies within the ink. However, it is not yet clear whether these morphologies persist upon thin film formation, that's to say upon drying of the catalyst ink [83,112]. As shown in a study by Berlinger *et al.* [83], morphological differences were observed between ionomer films formed from various n-propanol/water-content dispersions, suggesting the catalyst layer structure to be intrinsically sensitive to the ink dispersion medium. Catalyst layer structures and their links to catalyst ink morphologies are discussed in further details in paragraph 3.1.1.

From a practical point of view, the choice of solvent will usually depend on the targeted dispersion, ink and catalyst layer properties. In fact, the physical properties of a solvent greatly influence the physical properties of the ink [35]. Viscosity and surface tension of the solvent, and more broadly of the ink itself, will affect the ink coating process and thus the quality of the subsequent catalyst layer. A study by Park *et al.* [113] showed a linear correlation between ink viscosity and electrochemical performance of the resulting electrode. Targeted viscosity of the catalyst ink is also determined by the choice of coating process. In fact, depending on the coating method, different viscosities are required, as discussed in paragraph 3.2..

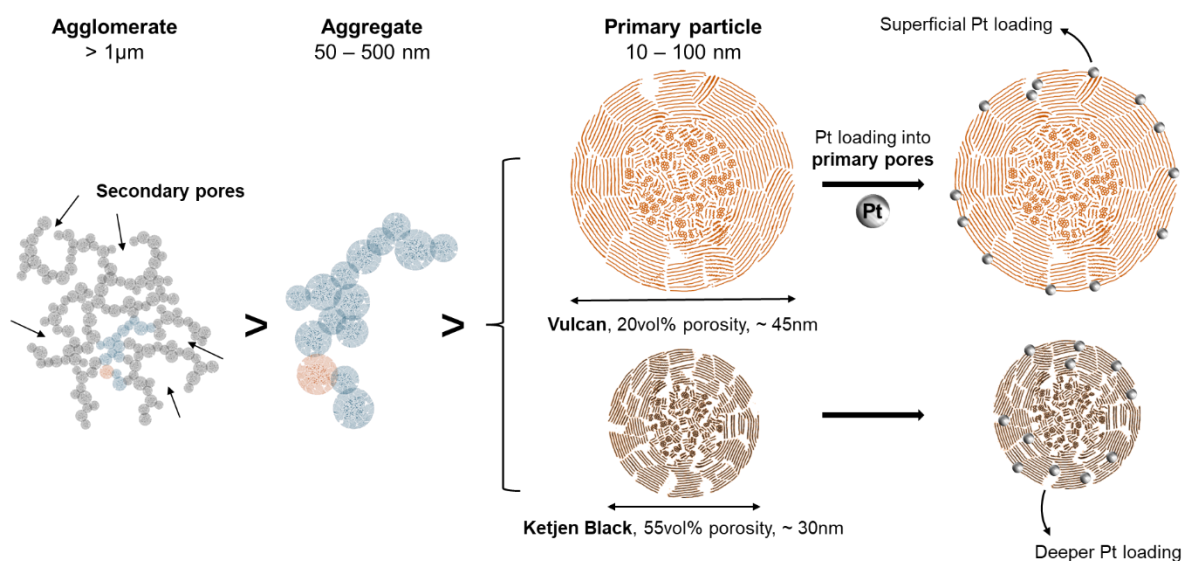
Dielectric constant is a controversial solvent parameter to consider. Many studies point to the dielectric constant having a direct effect on the ionomer and catalyst morphology within a solvent

[23,36,54]. For example, in a study on the rheology and structures of catalyst inks, Guo *et al.* [36] found that the size of catalyst agglomerates was reduced in solvents with higher dielectric constants, which also promoted ionomer adsorption onto catalyst particles, resulting in stronger ionomer/catalyst aggregates. But the correlation between dielectric constant and ionomer structure is not always experimentally observed, as exposed in a study by Park *et al.* [114]. In this study, several solvents were used to prepare catalyst inks. A linear correlation was made between the viscosity of the dispersions, the size of the aggregates and the performance of the cell, but no link was made with the dielectric constants of the solvents.

Usual solvents include aqueous and non-aqueous mixtures. Water/alcohol solutions, generally with 10 to 30 wt% of alcohol content [17,115,116] are commonly found as they are cheap, available and present low toxicity. Among them, water/propanol or water/ethanol mixes are the most popular [66,107,117]. Newer solvent mixtures have also shown promising results. For example, So *et al.* [108] obtained a better ionomer backbone solubility, thus smaller aggregates and a more homogeneous ionomer distribution with dipropylene glycol/water solutions. Moreover, Park *et al.* [113] reached higher MEA performance with propylene glycol-based ionomer dispersions than with water/alcohol-based ionomer dispersions. These results were explained by the ionomer forming a thicker layer onto the catalyst particles in propylene glycol-based inks, thus allowing for better proton conduction.

### 2.1.3. The catalyst

The reference catalyst used in the fabrication of PEMFCs catalyst layers is usually a system composed of Platinum (Pt) nanoparticles supported on amorphous carbon black. Common commercialized names are Vulcan XC 72 or Ketjen Black [8,23,118,119]. Carbon black provides a highly conductive porous surface for the Pt nanoparticles to be loaded onto, as illustrated by **Figure 4**. This loading grants a high surface area for the catalyst to interact with dioxygen and dihydrogen gas molecules. Gas molecules adsorb onto the Platinum through weak chemical bonds generated by interactions between the molecular orbitals of gases and the partially filled d-orbitals of Pt. This adsorption reduces the activation energy required to dissociate the atoms in the gas molecules, providing an activated site for reaction intermediates formation and stabilization. As a result, the oxidation of dihydrogen and the reduction of dioxygen are catalysed.



**Figure 4:** Carbon black powder structures and Platinum loading

Carbon black-supported Pt nanoparticle catalysts are mainly differentiated through their surface area and porosity [120]. For example, Vulcan XC 72 is characterized by a low porosity allowing for Pt particles to load on the outer surface, whereas Ketjen Black possesses a high surface area due to a higher porosity, allowing Pt particles on the inner pores [8,26,76], as differentiated on **Figure 4**. These specificities imply that slightly changing the properties of the carbon black used in the catalyst system will have an impact on the Platinum availability and capacity to interact with the reactants, as well as the adsorption behaviour of the ionomer [121–123]. In a study on the impact of carbon porosity on fuel cell performance, Yarlagadda *et al.* [121] concluded on the existence of an optimal porosity of the carbon black to ensure sufficient contact between the catalyst system and the reactants. In fact, the porosity of the carbon black particles should be sufficient to entrap Pt particles and shelter them from excessive ionomer coverage, but low enough to still permit dioxygen and proton passage towards the catalyst. However, as reported by Soboleva *et al.* [122], the structure of the carbon black particles tends to be highly irregular, making this optimal porosity hardly reachable and restraining it to a theoretical state.

The porosity of primary carbon black particles, as mentioned above, can be considered as the first scale of pores, known as primary pores, defined as the interspatial domains between the crystalline parts of the primary particle, where Pt nanoparticles will typically graft. The typical size of primary pores is smaller than 2 nm. The primary particles, which are about 1-100 nm wide [22,122,124], tend to form aggregates of typically 50-500 nm, which themselves stack upon one another to form micrometric agglomerates [122,125]. The space left between the primary carbon black particles within an aggregate or an agglomerate can either be referred to as mesopores [122] or as secondary pores [29,126]. These pores are typically smaller than 50 nm and are sites for concentrated ionomer adsorption [111]. Primary and secondary pores are schematized on **Figure 4**.

In terms of ionomer coverage of the catalyst particles, it is commonly seen in the literature that an ionomer thin film formation at the surface of the Pt-grafted carbon black particles is targeted [23,76,88]. This gives rise to a three-phase interface between the ionomer, the catalyst and the reactant gases, and translates experimentally to the creation of a ratio between the ionomer and catalyst contents (I/C ratio) [76,126,127] which is used to guide the formulation of catalyst inks and is generally comprised between 0 and 1. Several studies focus on the impact of the I/C ratio on the catalyst ink properties and fuel cell performance [111,128,129]. Generally speaking, the higher the I/C ratio, the more ionomer coverage on catalyst particles, even though there are variations depending on the carbon black and ionomer nature. Along the same logic as for the search for an optimal porosity of the carbon black particles, there is a theoretical optimal I/C ratio to ensure an ideal coating of the catalyst particles. In a study on the interparticle interaction within the catalyst ink, Mehrazi *et al.* [128] explored the impact of the I/C ratio on the electrode network formation. It was found that for a specific solvent mixture, under specific formulation conditions, there actually was an ideal I/C ratio of 0.75, providing the catalyst ink with best subsequent fuel cell performance. At 0.75 ratio, proton resistivity was minimized while carbon-carbon interaction was preserved, and the ionomer thin film was thick enough to reduce local oxygen transport resistance. This combination of properties ensured balance to reach the best performance in the given experimental conditions.

Interestingly, it is not yet clear in the literature whether the ratio of Pt on carbon black, also known as Pt loading, will impact ionomer adsorption onto the catalyst particles. As an example, Berlinger *et al.* [129] found that ionomer interaction was similar with either carbon black or Pt. These results suggest that due to the prevalence of carbon black surface over Pt surface within the medium, binding of the ionomer on the carbon black surface is the driving force in ionomer adsorption on catalyst particles. Contrariwise, it was found by Zhou *et al.* [130] that rheological properties of the catalyst ink were

highly dependent on the Pt loading of the carbon black particles, suggesting a strong impact of ionomer adsorption on Pt over the catalyst ink properties. Along the same lines, it was concluded by Owejan *et al.* [131] that both Pt loading and dispersion had an influence on the ionomer surface area coated onto the catalyst particles and thus, on mass transport resistance within the ionomer coating and consequently within the catalyst layer.

All in all, despite the nature of the dispersion medium remaining the most critical parameter in catalyst / ionomer interaction as explained in paragraph II-1-2, catalyst system characteristics also have an impact on ionomer adsorption capacity. A method was developed by Thoma *et al.* [132] to study the impact of formulation parameters on the adsorption behaviour of the ionomer onto the catalyst particles. This method consists in separating the free non-adsorbed ionomer in a sample from the adsorbed portion of ionomer through sedimentation of the catalyst particles and then quantifying the amount of non-adsorbed ionomer through thermogravimetric analysis. This method allows for the creation of a catalogue of various formulation parameters impacting on ionomer adsorption behaviour, providing an easy-to-read database. In this study, the impact of ionomer equivalent weight on the adsorption behaviour was studied; the methodology could be expanded to study the impact of catalyst system characteristics. Understanding the links between catalyst system morphology and catalyst ink properties also proves to be useful for fine tuning and optimizing catalyst ink formulation process. In this context, studies on shape-controlled catalysts, which tend to optimize available Pt surface, can be cited [8,133,134]. For example, Zhang *et al.* [133] engineered porous carbon nanotube microspheres, which multiplied oxygen reduction reaction activity by more than three in the prepared electrodes compared with electrodes prepared with non-porous carbon nanotube microspheres catalyst.

Optimization of the catalyst support is also a way of lowering the Platinum loading without impacting the catalysing capacity of the system. In fact, the cost of Pt utilization in PEMFCs has been a continuous issue throughout the years. Due to its scarcity, mining and production cost and because of the high industrial demand, Pt is one of the most expensive elements, accounting for nearly half the cost of PEMFC production [30]. A great amount of research on catalyst layer preparation is dedicated to reducing these costs [125]. As a result, Pt utilization within the catalyst layer has been increasingly optimized, reducing Pt loadings [5]. They progressively plummeted from 4 mg of Pt per cm<sup>2</sup> of catalyst layer to 0.4 mg/cm<sup>2</sup> in the late nineties [135,136]. Low-Pt loadings [125] are now considered to be below 0.2 mg/cm<sup>2</sup>, and ultra-low levels such as 0.014 mg/cm<sup>2</sup> have been reached [137]. Some research routes focus on optimizing Pt utilization through the enhancement of contact surface and carbon black support morphology. For example, the work of Zhu *et al.* [138] reports a new synthesis method towards more uniformly dispersed Pt onto carbon black supports. Working on the carbon support, Zhang *et al.* [133] designed carbon nanotubes to enhance the oxygen reduction reaction activity and minimize Pt oxidation.

Despite its clear popularity and efficiency in catalyst ink formulation, Pt is also prone to poisoning, degradation and contamination [139–142]. As explained in the review article by Shabani *et al.* [141], contaminant origins may be numerous, difficult to predict and alleviate. Contamination of catalyst layer components causes impairments on fuel cell operation and can be disastrous towards cell performance and lifetime. In order to reduce Pt degradation, some studies implemented the use of binary and ternary Pt-alloys as catalysts, as the non-noble metals may act as scavengers and protect Pt from degradation [21,25,39,143,144]. Thus, alloys such as PtNi, PtCo or PtNiMo can be seen in the literature, and superior stability and durability of these alloys over pure Pt to accelerated stress tests is generally reported, as is the case for PtCo catalyst in the study by Gatto *et al.* [25]. However, as observed by Li *et al.* [145] in a study on Co<sup>2+</sup> contamination of catalyst layers, the unavoidable

presence of contaminants upon long term utilization of the fuel cell ultimately results in catalyst degradation, which impairs the overall cell performance, especially at high current density. As a way of protecting the catalyst particles from poisoning and degradation while also enhancing reactant gas transport to the Pt surface, an innovative method was proposed by Hardisty *et al.* [146]. A Vanadium oxide coating is applied onto the catalyst particles through atomic layer deposition, forming a protective layer and improving the mass transport of hydrogen to the Pt surface.

Rather than optimizing Pt utilization as a catalyst, some studies focus on finding new Pt-free materials as a replacement [8,30,144,147]. As a result, reports of platinum-group-metal-free catalysts used in the fabrication of catalyst layers are found. For example, the possibility of using Cobalt as a fuel cell catalyst was investigated by Tasic *et al.* [30]. Electrochemical results showed that electrodeposited Cobalt onto the carbon black support could be used as a catalyst for fuel cell electrodes, thus reducing the cost of fabrication. Furthermore, the impact of platinum-group-metal-free catalysts on the bulk structures of the catalyst inks was studied by Khandavalli *et al.* [147], underlining the current need for better understanding of the interactions between the catalyst ink components. Overall, despite displaying promising results, Pt-free catalysts still lag behind classical pure Pt and Pt-alloy catalysts due to lower performance and complex fabrication processes, as pointed out by Jiao *et al.* [134].

## 2.2. Additives

As seen in the previous paragraphs, the ionomer, the solvent and the catalyst are the three essential components in the formulation of a catalyst ink. Additionally to these three main components, formulations may also include other species to help with chemical or physical properties. These additives may be divided into three categories. Firstly, they can be protective species here to prevent the catalyst layer components degradation. Secondly, they may be introduced to help enhance the overall electrode performance. Lastly, additives might be employed as a way of improving the physical integrity and durability of the catalyst layer.

In the category of protective additives, antioxidants are commonly found in catalyst inks [142,148]. Generally speaking, antioxidants act as electron-donating species either to prevent the formation of free radicals or interrupt the propagation of free radical reactions. Thus, antioxidants annihilate the noxious action and potential emergence of highly reactive free radicals. Within the antioxidants category, free radical scavengers are one specific subset that is commonly found in the literature on formulation additives for catalyst inks [149–151]. Free radical scavengers react directly with radical species through reversible redox reactions and transform them into less- or non-active molecules, preventing the radicals from reacting with the ionomer or the catalyst, preserving them from degradation. In other terms, they act as free-radical-neutralizers and are especially useful since they are highly specific in their action.

In practical terms, the most common radical species found within PEMFC operation are peroxide and oxygen radicals, which directly originate from the reactant gases, and may attack the reactive species within the cell, resulting in ionomer chain unzipping [46] or catalyst dissolution [142]. As an example, both Yook *et al.* [113] and Kim *et al.* [112] studied the antioxidant potential of CeOx nanotubes in MEAs. It was found that such carefully tailored nanomaterials both promoted catalyst stability and radical species scavenging by induction of a ligand effect through the interaction between Pt and CeOx. More common antioxidants can also be found, such as transition metal oxides which act as hydrogen peroxide decomposition catalysts, or Resveratrol<sup>®</sup> which is a commonly used polyphenol [148,152].

On top of protecting fuel cell components from free radical attacks, antioxidants can also play a role in the protection of catalyst particles from contamination and poisoning, as mentioned above with the

Vanadium oxide coating technique from Hardisty *et al.* [146]. Similarly to this method, Xie *et al.* [151] proposed a way of synthesizing Ta-TiO<sub>x</sub> nanoparticles onto the carbon black substrate to act as radical scavengers. This strategy resulted in a lowering of hydrogen peroxide yield and better preservation of current density compared to a fuel cell without scavengers. Despite antioxidants being the theoretical optimal solution towards protection of fuel cell components from degradation, studies show that long-term fuel cell operation ultimately displaces the challenge onto antioxidant degradation [148]. Thus, their use should be carefully planned and their impact on the overall fuel cell properties and materials degradation mechanisms acknowledged.

Regarding the use of additives towards electrode performance improvement, it usually consists in the use of specific additional chemical species as a path to tailoring the catalyst layer structure in a way that favours the electrochemical reactions at the three-phase interface. Along this line, pore formers have been used for several decades in the fabrication of fuel cell electrodes [47,153,154]. Their chemical nature is variable. From ammonium salts [153], to polyvinyl alcohol [154] for example, they act as sacrificial mass content, that is to say they will be removed from the final catalyst layer, either by solubilization or chemical decomposition [5]. Usually, increasing the catalyst layer porosity will promote gas mass transport during fuel cell operation. However, pore forming agents should be used in moderate amounts for their overuse may interfere with electron and proton transport rates [47]. On top of increasing the macroporosity of the catalyst layer, pore formers can also be employed to directly modify the three-phase interface. In fact, in a study on the use of polyvinyl alcohol as a pore forming agent, Cheng *et al.* [154] reported the creation of pores within the ionomer thin layer on the catalyst particles, which allowed for a better accessibility of the active reaction sites during cell operation, thus improving local oxygen transport in the cathode catalyst layer, resulting in a global cell performance improvement.

Some studies report the improvement of electrode performance through the use of additive content as a mass transport enhancer [48,155]. As an example, in a study by Lee *et al.* [155], low molecular weight polyethylene glycol was employed into catalyst ink formulation to improve the electrode performance at high current density. However, no explanation as to how polyethylene glycol acted to enhance mass transport was given, and it was also reported that the use of high molecular weight polyethylene glycol had the opposite effect, lowering the ionomer conductivity. Overall, such as with the use of pore formers, mass transport enhancers should be carefully selected, and their efficacy seems to be difficult to predict.

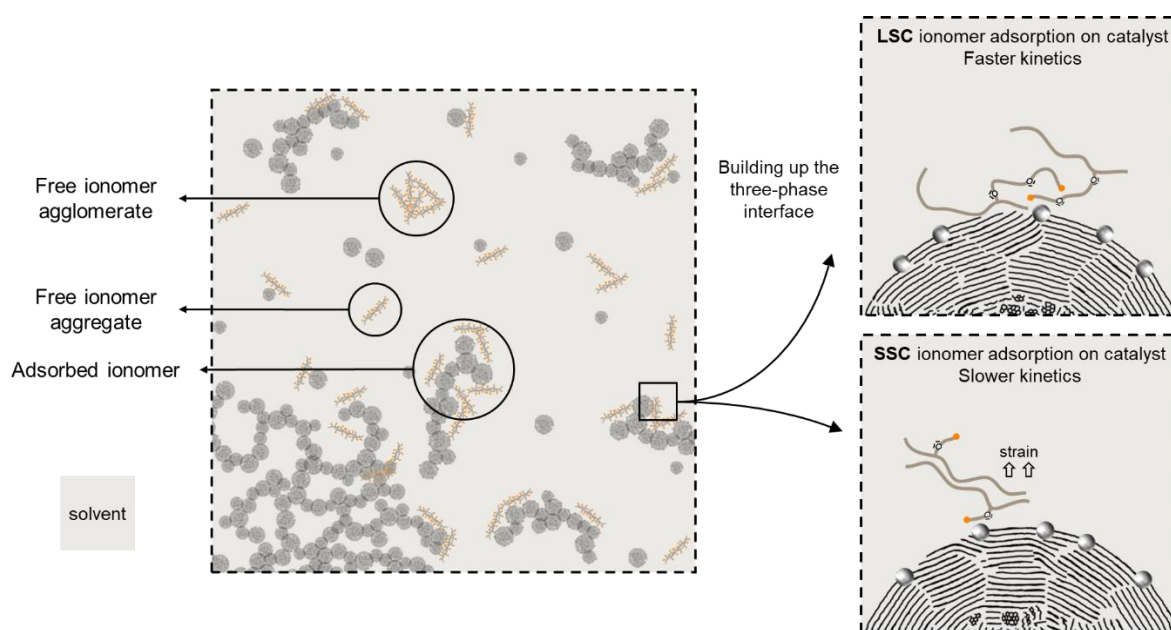
Concerning the enhancement of the catalyst layer physical and mechanical integrity, the common targeted use of additives is the improvement of both the global catalyst ink stability and the resulting catalyst layer resistance to mechanical stress [156–158]. Catalyst ink stability is globally governed by the ionomer-induced steric repulsion which occurs between the catalyst aggregates. However, it can be improved by adding a charged dispersant which will further increase electrostatic repulsion on the aggregates surface and have an impact on the rheological properties of the ink. For example, in a study by So *et al.* [156], a commercial dispersant was shown to induce shear thinning and fast viscosity recovery of a catalyst ink formulation, which was equated to having a more stable dispersion with more stable coating properties. Catalyst layer resistance to mechanical stress is usually detected from the drying stage with the formation of cracks during the solvent evaporation process. Cracking of the catalyst layer is considered to be affected by the interactions between the ionomer, catalyst and solvent. Hence, crack formation is influenced by the choice of the dispersing solvent and of the ionomer. The presence of cracks decreases the mechanical durability of the catalyst layer and exposes them to acute flooding during operation [159,160], thus prevention of cracks formation is crucial. The use of additives is reported to be a way of reducing cracking without having to sacrifice the chosen

solvent / ionomer combination [157,158]. Addition of a high boiling point solvent was reported in a study by Hasegawa *et al.* [157] to reduce crack formation during the drying process by inducing a milder drying rate. Another route was investigated by Liu *et al.* [158] with the use of benzoic acid as a way of promoting attractive interactions between the catalyst particles without causing their aggregation, thus inhibiting cracking.

All in all, additives can prove to be useful in catalyst ink formulation as they may serve as protecting agents, performance boosters or structure strengtheners. The reports on additives nonetheless remain more of tailored solutions to unique experimental conditions and settings than general purpose recommendations, since the experimental studies on their impact on catalyst layer fabrication are scarce and highly specific.

### 2.3. The formulation method

A correct dispersion of the components of the ink is necessary to ensure a stable and homogeneous product [35]. As seen previously in this chapter, the catalyst and the ionomer tend to form more or less agglomerated structures when added to a solvent. Ink dispersion is meant to ensure sufficient breakage of the agglomerates, thus allowing improved interactions between the ionomer and the catalyst and also ensure the reproducibility of the behaviour of the inks [161], as schematized on **Figure 5**. Numerous dispersion methods are available and shown to result in inks with different physical properties [162]. The purpose of this section is to provide a brief overview on the existing dispersion techniques and their practical implications on catalyst ink formulation, revealing the challenges faced when choosing a dispersion process, with the objective to complete review articles already found in literature more focused on presenting the dispersion methods.



**Figure 5:** Schematic representation of structures and interactions within the catalyst ink

Breakage of the agglomerates within the catalyst ink requires an energy input. This energy can be given from various sources, whether it be by applying ultrasounds, mechanical energy or even pressure. The following paragraphs provide a summary of the preponderant dispersion methods used with catalyst inks, categorized by the nature of energy at play, and give the main implications arising from each category.

First, sonication can be mentioned as one of the most popular dispersion methods [26,163]. Ultrasonic waves are widely used as a soft dispersing method, which can be found either as bath or tip sonication. Bath sonication consists in the immersion of the sample to be dispersed in a thermoregulated water (or other liquid) bath. This bath generates ultrasonic sound waves, which give rise to a cavitation phenomenon, where microscopic bubbles are rapidly created and collapsed, resulting in microscopic high-intensity shock waves all throughout the sample volume, and the subsequent breakage and dispersion of carbon agglomerates. Tip sonication on the other hand, albeit based on the same cavitation phenomena, relies on a vibrating rod submerged directly into the sample, thus allowing for a more intense and localized sonication. Sonication, especially bath sonication, is said to be a soft dispersion method, allowing the breakage of large carbon aggregates without detaching Pt nanoparticles [163]. However, ultrasonic parameters must be thought of and chosen according to the desired dispersion state of the final catalyst ink. In fact, the use of sonication does not guarantee an ideal dispersion, independently of the other formulation parameters such as ionomer content, catalyst nature or solvent choice. Some studies reveal that dispersion through sonication bath may not be sufficient to break smaller carbon agglomerates back into primary particles [164], whereas the use of tip sonication can prove to be too aggressive, to the point where reverse agglomeration may be induced or even Pt nanoparticles may be detached or dissolved [161,164]. In a study on the impact of catalyst ink dispersing method on fuel cell performance, Du *et al.* [163] showed that combining a short preliminary tip sonication step with a subsequent longer bath sonication allowed for an optimal way of breaking the carbon agglomerates into primary particles without detaching Pt nanoparticles. Moreover, beyond dispersing agglomerates, sonication has also been shown to grant stability to the catalyst ink when sufficiently strong. A study by Xie *et al.* [165] revealed that breakage of carbon agglomerates was not the only goal of an efficient ultrasonic dispersion. In fact, it also had to be powerful enough to further disperse the ionomer clusters into the slurry, resulting in a strengthened ionomer network. As a result, an increase in the ink viscosity and an attenuation of the ink sedimentation rate would provide a more stable ink.

Energy input can also be brought to the catalyst ink by mechanical forces. Among mechanical methods, ball milling, also known as jar roller milling [166], is frequently used for its easy scalability to industrial levels [116,162,163]. During ball milling, the catalyst ink to be dispersed is poured into a cylindrical or spherical milling chamber containing beads which are, most of the time, fabricated in zirconium [162,163]. Rotation of the chamber then allows for mechanical energy to be transferred on the ink through friction, collision and squeezing between the beads, resulting in the grinding and mixing of agglomerates in the catalyst ink. Usually, as with ultrasonication, quality of the dispersion after ball milling is evaluated through ink viscosity and rheological behaviour. An increase in viscosity and shear thinning behaviour are expected for an ink to be considered well dispersed, which is also advantageous for the following coating process of the catalyst ink [35,163]. In a study on the effect of ball milling time on ink and catalyst layer microstructure, Baez-Cotto *et al.* [166] reported a correlation between mixing time, ink viscosity and crack formation in the catalyst layer. It was found that excessive grinding of the catalyst ink resulted in a loss of shear thinning behaviour and that the associated excessively monodisperse ink particle distribution was a weakening factor for interparticle interaction, promoting crack formation during the catalyst layer drying step. Thus, ball milling time and rotation speed must be controlled in order not to overgrind the catalyst ink slurry and deteriorate the ink properties, as shown with cryogenic transmission electron microscopy observations by Takahashi *et al.* [167]. Furthermore, as shown by Bu *et al.* [168], the presence of an external element, for instance the Zirconium beads, may be a source of cross contamination of the ink during the milling process. The same problem is encountered when working with magnetic or mechanical rod stirrers, which in addition, prove to be less efficient than ball milling or ultrasonication in terms of aggregate breakage

and ink stability [87]. Mechanical dispersion without the use of an external energy transfer agent can be achieved using planetary mixers, in which the mixing tool rotates on its own axis while simultaneously revolving around the central axis of the container [162,169]. This method was nonetheless shown to result in the least efficient dispersion of the ink in a study by Yang *et al.* [162], compared with ball milling, ultrasonication and pressure homogenization. In fact, out of the four tested formulations in this study, the ink dispersed by planetary mixer had the least viscosity enhancement, the largest remaining aggregates, and the subsequent catalyst layer fabricated from this ink presented the most cracked surface.

As mentioned just above, a third possibility is to use pressure to achieve the dispersion of agglomerates within the catalyst ink. High pressure homogenizers can quickly reduce the size of the aggregates by pushing the catalyst ink through a microscopic constriction, resulting in localized high shear. Although theoretically more efficient than sonication, high pressure homogenization is a less popular dispersing method [26,116,162]. In fact, on top of requiring tremendous amounts of power to be applied, it is also hardly scalable to industrial processes and remains confined to lab scale studies. In a study by Yang *et al.*<sup>161</sup>, the ink prepared via high pressure homogenization was the one with the most enhanced ink properties compared with the ink prepared through ultrasonication, ball milling or planetary mixer, which demonstrates the higher mixing efficiency of this method. Nevertheless, the catalyst layer obtained from this ink yielded the lowest electrochemical performance from polarization curves, and it was underlined that the heat produced during high pressure homogenization due to the high intensity of the shear could give rise to adverse effects, such as reverse aggregation or deterioration of the ink components.

Dispersion methods can be used as complementary to one another. This is known as the dual dispersion method. It has been seen in previous paragraphs that bath sonication could be coupled to tip sonication for process optimization. Ball milling may also be followed by sonication, as shown in a study by Liu *et al.* [170], to lead to a more stable ink. When choosing a dispersion process, literature seems to point to rheology and stability of the dispersed catalyst ink as the relevant factors to account for the method efficacy, since the dispersion methods used have been linked to the quality of the coating obtained during catalyst layer fabrication [171]. Moreover, only few studies have examined the influence of the order of mixing of the components on the ink and catalyst layer properties. Yet, it has been observed by Carine *et al.* [169] that the order in which the components were introduced into the formulation had an impact on particle sizes within the ink and on its apparent viscosity. Another illustration of the importance of the order of mixing can be found in a study by Sun *et al.* [172], who concluded that adding the ionomer directly onto the catalyst particles without primary dilution in the solvent led to a higher probability of detaching Pt nanoparticles from their carbon black support. This is detrimental to the ink since free Pt particles tend to aggregate, reducing the potential catalyst surface and facilitating defects formation during the catalyst layer drying step.

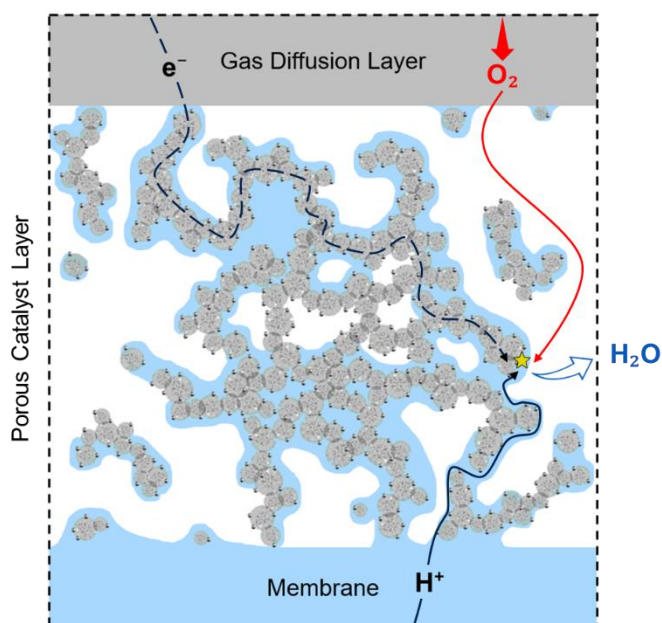
Finally, the adsorption behaviour of the ionomer onto the catalyst particles has been consistently shown to have slow kinetics [67,110], making catalyst inks metastable systems, as seen in previous paragraphs along this review. Thus, even though the dispersion process may have been optimized to result in the best ink properties, aging of the catalyst ink is still to be kept in mind for further use of the prepared slurry [56,173–175].

### 3. Catalyst layer preparation process

As seen in the previous chapter of this review, catalyst ink preparation requires precise considerations when it comes to choosing the formulation parameters, whether it be on the nature of the components, the physical interactions between them, or the implications of the dispersing step. The purpose of the so-prepared catalyst ink is to be deposited onto a substrate and then dried, resulting in the formation of the catalyst layer. The ink can either be spread onto the proton exchange membrane or the gas diffusion layer, depending on the choice of coating method. The main challenge arising during the transition from the catalyst ink to a catalyst layer is to maintain the interactions between the ionomer and the catalyst whilst also creating a homogenous and adequate porosity within the layer to allow for mass transport. In this section, the issues faced during this transition from formulation to material are highlighted. The focus is made on revealing the links between the final structural and transport properties of the catalyst layer, the choice of ink deposition technique and of drying method, in order to grasp and untie the complexities of the catalyst layer preparation process.

#### 3.1. Targeted catalyst layer properties

Several roles are to be ensured by the catalyst layer for the fuel cell to work in optimal conditions [112], as illustrated by **Figure 6**. First and foremost, transport properties are crucial and can be divided into two categories: mass and charge transport. On the one hand, mass transport must be efficient for the cell performance to be guaranteed. Reactant gases must be transported from the gas inlets to the reaction sites at the heart of the catalyst layer, whereas the water byproduct must be managed. On the other hand, charge transport ought to go uninterrupted for the cell to deliver an electrical current. Both protons and electrons must be led, either from the membrane or the gas diffusion layer respectively, to the reaction sites where they will meet with the reactants. Guarantee of these transport properties and their optimization is possible through modifications of the structure of the catalyst layer [112]. Thus, design of the final catalyst layer micro- and macro-structure is concomitantly important to transport properties for fuel cell operation and will be discussed hereafter.



**Figure 6:** Schematic representation of the phenomena within the catalyst layer in an operating electrode

### 3.1.1. Structural properties of the catalyst layer

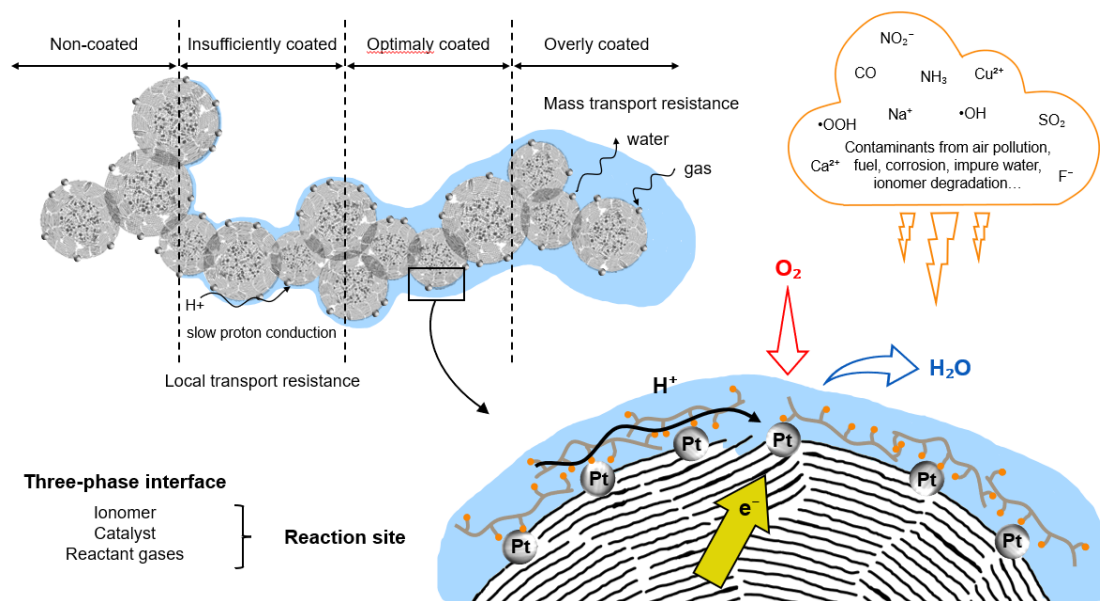
Assessment of the final catalyst layer structure is done on a multiscale observation. At the macrostructure level, parameters such as layer porosity, thickness, surface roughness, or adhesion to the substrate can be examined to evaluate the quality of a catalyst layer [7,22,23]. Targeted values can be dependent on the technical requirements and specificities of each fabrication process [23], but some orders of magnitude can be found. For example, catalyst layers thicknesses of 5 to a few dozen micrometers are reported, while overall porosities are generally found between 40 and 70% [22,23].

At the microstructure level, quality assessment of the catalyst layer consists in determining whether the arrangement of the catalyst layer components is such that the three-phase interface between the ionomer, the catalyst particles and the reactant gases remains maximized [122,176,177]. Thus, micro- and nano-pore structures are usually analysed and ionomer thin film thickness, catalyst aggregates size and dispersion state are measured using electronic microscopy techniques most of the times [88,116,122]. What is generally sought in micrographs is a homogeneous dispersion of intact catalyst aggregates back as close as possible to primary particles, connected through a few nanometers thick ionomer thin film coating [88,116,122].

Moreover, this final catalyst layer structure has consistently been shown to be drastically impacted by the formulation process of the catalyst ink [113,116,172,178], hence the importance of taking it into account when designing the ink formulation methods. For example, it was shown by Park *et al.* [113] that the solvent composition of the ink had an influence on the final catalyst layer micro-structure. More precisely, the thickness of the ionomer thin film was found to be linked to the water / alcohol solvent ratio, increasing with the alcohol content. On a more global point of view, Sun *et al.* [172] stated that the structure of the catalyst layer was governed by catalyst-ionomer interactions through the ionomer capacity to adsorb onto the catalyst particles, which was itself influenced by the overall ink composition and formulation process. More recently, Ren *et al.* [178] proposed a rationalization of the catalyst layer microstructure formation mechanism, which was found to be directly linked to ink composition, properties and preliminary structures. Similar work has been done by Lee *et al.* [123] in an investigation on catalyst layer structure formation through ink droplet drying analysis. These studies allow for a better understanding of the physico-chemical phenomena at play during the transition from catalyst ink to catalyst layer and help orient choices for ink formulation.

Concerning rationalization of mechanisms and prediction of structure formation, numerous numerical simulations can be found in the literature [179–181]. In fact, molecular dynamics tools turn out to be particularly useful in this case since they may help avoid unnecessary experimental testing and boost productivity. For example, Dorenbos *et al.* [179] used coarse-grained dissipative particle dynamics in order to predict the formation of pore networks within the catalyst layer and the subsequent water and proton pathways. Not only did this study allow for fast estimation of the water diffusion constants, but it also helped draw a counterintuitive hypothesis according to which smaller pores led to greater water diffusion, which was then experimentally verified. The use of molecular dynamics simulation method in a study by Kang *et al.* [181] allowed for the modelling of the impact of catalyst layer preparation on the final catalyst layer structure and its link to mass phase repartition during cell operation. More specifically, it was found that the distribution of constituents within the operating catalyst layer was not homogeneous at the nanoscopic level. In fact, water molecules and other polar groups were found to concentrate at the Pt surface, whereas most of the ionomer backbone was drawn to the carbon. These findings helped understanding the impact of Pt loading on catalyst layer nanostructures, as discussed in paragraph 2.1.3.

### 3.1.2. Mass transport phenomena



**Figure 7:** Schematization of the ionomer thin film and the three-phase interface

The link between catalyst ink formulation and catalyst layer structures was underlined in the first paragraphs of this section. As highlighted in the next few lines of this section, and illustrated by **Figure 7**, the final catalyst layer structure then plays a crucial role in dictating both mass and local transport properties within the operating electrode. Mass transport phenomenon is observed through cell operation within the MEA [182]. Reactant gases are transported near the reaction sites and must be adequately managed in order to ensure reaction rates. In fact, gas transport is an issue tackled by numerous studies [126,131,155,182–186], many of which focus on analysing the effect of experimental parameters on the overall gas transport resistance. For example, in a study on mass transport resistance in catalyst layers prepared via electrospray deposition, Conde *et al.* [182] observed the influence of catalyst nature and concentration, which resulted in the establishment of an optimal catalyst utilization linked to a precise catalyst layer thickness. For instance, for layers prepared with Pt/C 20 wt% catalyst, an optimal Pt loading of 0.17 mgPt·cm<sup>-2</sup> was found at which ionic conductivity, mass transport and overall catalyst utilization were optimal. This Pt loading corresponded to a catalyst layer thickness of 18 μm. These studies underline the fact that, as for the preparation of the catalyst ink, there is no universal answer as to how the experimental parameters should be chosen to achieve perfect gas transport. There are, however, general considerations to be made regarding the impact of the catalyst layer components and structures on mass transport phenomena.

Structural parameters of the catalyst layer are of prime importance for gas transport. *Salari et al.* [126] showed that both the size of primary pores and the overall catalyst layer porosity had an impact on oxygen diffusion resistance. More precisely, oxygen diffusion was improved for an increased catalyst layer porosity and bigger primary pores, basically showing that gases need sufficient free space to move towards reaction sites.

The macro-, micro- and nano structures within the catalyst layer are nonetheless not the only factors of impact on gas diffusivity. In fact, the progressive reduction of Pt loadings in the fabrication of catalyst layers, as seen in the Section 2 of this review, has also contributed to this issue [183]. Several studies revealed that the lower the Pt loading, the higher the gas transport resistance in catalyst layers [131,185,186]. This effect has been attributed to the loss of effective Pt surface area resulting in gas transport limitations.

Some solutions have been proposed to counter gas transport resistance. As seen in Section 2 of this review, additives can act as mass transport enhancers. For example, *Lee et al.* [155] managed to reduce mass transport resistance by adding polyethylene glycol into their ink formulation. However, by doing so, an increase in proton transport resistance was also observed, which was attributed to a decrease in ionomer activity on account of polyethylene glycol, underlining the intertwining and potentially contradictory effects of the experimental parameters. Furthermore, *Conde et al.* [182] observed that the ink deposition method choice also played a role in mass transport resistance. The impact of ink coating technique on the catalyst layer is explained in further details in the next part of this Section. Gas (and overall mass) transport can also be improved by novel ionomer immobilization techniques, as explained by *Choi et al.* [187].

Once again, computational methods prove to be an effective tool for prediction and analysis of mass transport within the catalyst layer, as discussed in studies by *Ohma et al.* [185], *Shin et al.* [184] or by *Mashio et al.* [183], in which various models are proposed to describe transport phenomena taking into account various parameters such as effective catalyst surface area, average pore diameters or ionomer chemical structure.

As stated in the introductory paragraph of this section, management of liquid water production from the redox reaction constitutes the second half of the mass transport issue within the catalyst layer. An optimal water content needs to be reached and maintained in the catalyst layer [188,189], as excess water leads to flooding whereas drought hinders protonic conductivity. More precisely, water accumulation in the fuel cell is caused by the combination of electrochemical production through the redox reaction and electro-osmotic drag transport [190] generated by the movement of Hydrogen ions under the influence of the cell electric field. As a result, a water concentration gradient is observed across the MEA and back diffusion of water occurs from the cathode to the anode. Consequently, the anode side of the membrane tends to dry out, whereas the cathode side is prone to flooding, as shown in a study by *Toudret et al.* [191].

Just as it is the case for gas transport, water transport within the catalyst layer is extensively studied [29,191–196], and the importance of catalyst layer structure in this transport is often underlined. In fact, the interplay between hydrophilic and hydrophobic domains arising from the nature of the catalyst layer components are reported to complicate the dynamics of water transport generated during cell operation [29]. More precisely, it was found by *Fathi et al.* [192] in a study on the modelling of phase flows in a cathode catalyst layer that within the hydrophobic domains of the catalyst layer the larger pores were preferentially flooded, whereas water transport was more efficient through smaller pores within the hydrophilic domains. Along the same lines, it was reported by *Tesfaye et al.* [195] that the orientation of the ionomer chains within the ionomer thin film was a contributing factor to both water transport and swelling behaviour. More precisely, it was found that water transport was slowed by the parallel orientation of the film's nanostructures to the surface. This behaviour was said to dictate thin film thickness and consequently affect oxygen transport and proton conduction [88,192,195]. Moreover, swelling of the ionomer thin film in the absence of solvent could be due to a confinement effect, as mentioned by *Weber and Kusoglu* [196], where the random orientation of the ionomer chains is compromised by physical hindrance within the catalyst layer.

Mentions of Schröder's paradox in the literature on water transport in PEMFCs are often being made in an attempt to elucidate the phenomena at play [193,194]. Schröder's paradox describes the fact that despite the thermodynamic equilibrium between liquid water and saturated vapor, certain polymers tend to have different maximum water uptake in those two phases. This implies inhomogeneous interactions between ionomer and water which may affect the swelling behaviour of ionomer thin film, thus reinforcing the effects described in the previous paragraph.

### 3.1.3. Local transport phenomena

Finally, the mass transport of reactants and the water byproduct coupled with structural properties of the catalyst layer partake in charge conduction and resistance, hence transport phenomena must be considered at the local scale as well. Protons ought to be carried out from the membrane and electrons travel from the gas diffusion layer to meet at the reaction sites at the three-phase interface between the ionomer, the catalyst particles and the reactant gases. The ionomer matrix constitutes the proton conduction network in that the ionomer thin film allows for a continuous conductive path through the catalyst layer, while electron conduction occurs through carbon black transportation [112].

These local transport phenomena are normally spontaneous considering the electrical conduction circuit created with PEMFC operation. However, as explained in the previous paragraphs, this sole functioning of the cell gives rise to mass transport phenomena, and is especially impactful on water transport, resulting in a double-edge sword effect since unfavourable out-turns may then occur back onto proton and electron conduction [186]. In fact, it was shown by Eskandari *et al.* [124] in a study on the effects of ionomer thin film hydration on proton conductivity that the ionomer thin film water content was directly correlated to proton conduction capacity of the ionomer thin film and dependent on the ionomer equivalent weight through its acid content. Moreover, it was shown that low-EW-ionomers presented enhanced proton conductivity compared with high-EW-ionomers, underlining the advantage of SSC PFSA ionomers over LSC PFSA ionomers.

Several review articles report the use of activation mechanisms to promote charge transfer without decreasing mass transport [7,177,197,198]. They can be of various nature, whether it be thermal treatments during the formulation of the catalyst ink, or post-fabrication off-line treatments. As an example, electrode or MEA boiling [7,50] consists in submitting the electrode to a steam environment for a few minutes, enhancing the porosity, washing away some unbound impurities or excess ionomer, thus improving the cell performance. Efforts can also be made in order to boost mass transport at the local level, such as with the use of pore formers, which were cited in Section II of this review. For example, Cheng *et al.* [154] managed to enhance local oxygen transport by designing a nano porosity within the ionomer thin film through the use of polyvinyl alcohol as a sacrificial additive.

Finally, analysis of computational predictions of transport properties obtained through numerical simulations is a way to gain in hindsight and spot weaker or passive regions of the electrode. Hence, many models have been proposed to study the impact of experimental parameters on transport properties, reaction rates and electrode performance [184,199,200].

## 3.2. The coating process

As for all the other parameters in the catalyst ink preparation process, the choices for ink deposition techniques are numerous and diversely impactful to the resulting catalyst ink layer and the subsequently dried catalyst layer [8,26,201–205]. The choice of coating process will also depend on the catalyst ink properties such as ink viscosity or intrinsic solvent evaporation rate, for different methods require different ink specifications to be operated, and two different catalyst inks will lead to two catalyst layers with differing properties through the same coating process [204].

Catalyst ink deposition methods can be divided into two groups, namely the spraying and printing techniques for which the required properties of the primary catalyst ink differ greatly. Techniques under the spraying category generally involve rapid projection of liquid catalyst ink droplets, thus necessitating relatively low viscosity slurries [206]. Electrospray deposition is a popular spraying method, where high voltage is applied to a nozzle containing the catalyst ink in order to create an electrical field which ionizes the ink. This causes the ionized ink to break into charged droplets, which

are then accelerated by the difference of potential between the electrified nozzle and the substrate onto which they are deposited [182,207]. Electro spray deposition technique is particularly useful to manufacture low-defects homogeneous ultrathin catalyst layers. This method also allows for multiple coatings of many thin layers, producing overlapped layers of ionomer which maximizes the proton conduction ability of the catalyst layer [182]. Furthermore, due to the arrangement of droplets, electro spray deposition confers superhydrophobic properties to the catalyst layer which are beneficial to water management during fuel cell operation [207]. The use of this technique nevertheless requires the substrate to be semiconductor in order for the catalyst ink layer to avoid being charged by the end of the procedure and is generally not adapted to high-solid-content catalyst inks [182].

The ultrasonic spray deposition technique, also known as inkjet printing, is quite similar in terms of the quality of the produced film [40,208]. In this case, the catalyst ink is atomized into droplets through the effect of ultrasonic waves whose frequency affects droplets size. The droplets are then transported to the substrate by a carrier gas whose flow rate is modulated to control film thickness [209–211]. This method is reported to enhance Pt utilization thanks to a better distribution compared with non-spraying methods [209]. However, as concluded by Turtayeva *et al.* [211], the state and properties of the catalyst layer obtained via ultrasonic spray deposition are sensitive to a myriad of experimental parameters, such as the catalyst nature and shelf life, which have been shown to influence the thickness and homogeneity of the coating, resulting in catalyst layers of dissimilar properties.

The use of atomic layer deposition is also reported in the fabrication of catalyst layers [212–214]. It relies on a self-limiting chemical reaction to result in the stacking of atomic layers which will form a thin film. The substrate to be coated is exposed to a gaseous precursor, which will react to form a precursor monolayer. After a first purge, the monolayer is put in contact with a second precursor to form the first coating layer through reaction with the first precursor monolayer [214]. By definition, this coating method cannot be used to directly deposit the catalyst ink onto the substrate. However, it is often used to produce Pt coated catalyst particles [212], and this process can be diverted to help in catalyst ink coating process, as shown in a study by Dull *et al.* [213]. In this study, Dull *et al.* got rid of the catalyst ink formulation step, and reconstructed a catalyst layer component by component. A first layer of carbon was deposited onto the gas diffusion layer; atomic layer deposition was then used to coat the carbon with Pt particles, and this so-created catalyst system was finally impregnated with an ionomer dispersion.

Among alternative coating processes, reactive spray deposition technology can also be cited as a catalyst deposition method [8,215,216]. With this method, a precursor solution is atomized through spraying into a reactive environment where it will react to form the desired nanoparticles before colliding onto the substrate [8]. These alternative fabrication paths are reported to help with ionomer coverage and prevention of catalyst corrosion, thus improving the durability of the catalyst layer [215,216].

Electrospinning is a hybrid method between spraying and printing. It is a fibre fabrication method utilizing a high voltage electric field to stack the fibres onto a substrate in an organized or random pattern and allowing for solvent evaporation upon travel from the printing nozzle to the substrate [8]. Electrospinning can be used in catalyst layer fabrication utilizing catalyst ink as the electrospun fluid being made into nanometric fibres [44,217,218]. For example, Chan *et al.* [44] produced a fuel cell catalyst layer from a carbon nanofiber-based catalyst ink. It was shown through electronic microscopy that this method yielded ionomer coated catalyst fibres and ionomer bridges between those fibres, allowing for a highly proton-conductive structure and heightened electrical performances, but increased gas transport resistance due to the prevalence of ionomer surface within the layer and relatively low porosity.

While spraying techniques are advantageous for producing catalyst ink coatings with finely tuned thickness and homogeneity, ink printing methods may be more suitable for high solid content and more viscous catalyst inks [8]. Moreover, for any spraying method, the choice of solvent for the catalyst ink must be tailored in such a way that ensures it will not evaporate during spraying, risking nozzle obstruction. Hence, printing techniques generally offer greater formulation freedom in the choice of components and catalyst ink properties requirements for operation.

Printing the catalyst ink coating can either be a direct or indirect process [205]. During a direct printing process, as for the spraying methods mentioned above, the catalyst ink is spread directly onto the gas diffusion layer or the membrane, whereas for an indirect printing process, an intermediate substrate is used for the primary coating of the catalyst ink layer, which then undergoes either drying or other treatments before being merged into the MEA.

Direct printing methods offer the advantage of lessening the number of fabrication steps and providing catalyst layers with better adhesion to their substrate [202]. The screen-printing technique is a common direct printing method, during which the catalyst ink is passed through a mesh with the help of a doctor blade to form a layer directly onto either the gas diffusion layer or the substrate [53]. This is a rapid, discontinuous method that allows the use of highly viscous inks. However, the catalyst layer properties obtained from this method are reported to be strongly dependent on the solvent used for the formulation of the catalyst ink [53,203]. For example, in a study on the use of flatbed screen printing for the fabrication of catalyst layers, Ney *et al.* [203] observed that solvent evaporation was a critical parameter of the process, influencing both the catalyst ink layer stability and Pt loading.

Inkjet printing is a more meticulous printing method, where micrometric droplets of catalyst ink are deposited one after the other onto the substrate, permitting a more precise control of the substrate surface coverage, layer thickness and pattern [52,202,219]. It however tends to be a less suitable method for highly viscous inks, with the main risk being once again clogging of the printing nozzle. Solvent evaporation issues may also be encountered because there is a delay between the deposition of the first droplet and completion of the printing [219]. Moreover, it was shown in a study by Tamaki *et al.* [52] that catalyst layers prepared via inkjet printing were subject to ionomer distribution inhomogeneities, as well as crack formation upon drying.

Indirect printing methods can be a way of adapting the catalyst ink layer properties before forming the final MEA. Roll-to-roll manufacturing is a particularly popular indirect continuous printing process, where the catalyst ink film is first deposited onto an intermediate substrate via a primary coating method, before being transferred onto the gas diffusion layer or the membrane [26]. The primary coating method must be adapted to the continuous manufacturing process. Thus, slot-die and doctor blade coating are generally employed.

For slot-die coating, the entry of a catalyst ink reservoir is equipped with a narrow slit and positioned above the intermediate substrate, allowing the continuous deposition of a thin catalyst ink layer [26,201,204]. As shown by Creel *et al.* [201], the uniformity of the formed thin ink layer is dependent on experimental coating parameters, such as distance between the slit and the substrate, slit width, substrate speed or pressure within the reservoir. Thin film homogeneity is also shown to be influenced by catalyst ink properties and rheology.

Doctor-blade coating is quite similar to slot-die coating in that a thin catalyst ink layer is also continuously spread onto the substrate. Under this process, the catalyst ink is poured in front of the doctor-blade onto the substrate, the latter of which then translates for the ink to be passed under the doctor-blade, thus resulting in a thin catalyst ink layer [220]. Doctor-blade and slot-die coating may also be employed as direct coating methods, applying the catalyst ink directly onto the gas diffusion

layer or the membrane, but as for screen printing, only few modifications of the layer can then be made before drying. However, these methods present the advantage of being easily scalable to industrial processes [220].

Decal transfer is the non-continuous equivalent to roll-to-roll manufacturing. The catalyst ink thin layer is first deposited onto an intermediate substrate via a chosen coating method. Then, the catalyst ink layer is dried prior to its transfer to the ionomer membrane and assembly with the rest of the MEA, generally via hot-pressing [117,202]. As shown by Jung *et al.* [117], decal transfer is a low interfacial resistance coating method providing homogeneous and low-defects catalyst layers under the condition of finding the optimum catalyst ink formulation.

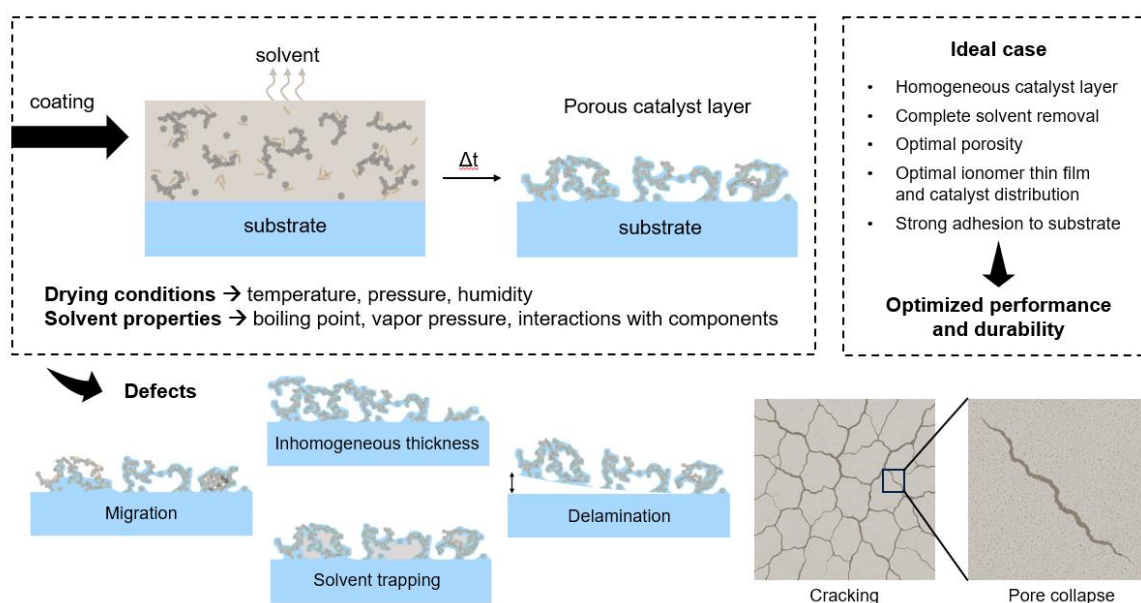
As seen in this section, the coating processes are of various nature and can require very different ink properties, homogeneity and stability. Potential structural modifications of the catalyst ink thin layer can be made during indirect coating processes, but the quality of the fabricated catalyst layer is highly variable and dependent on every experimental parameter. The choice of coating process often implies necessary modifications on the catalyst ink formulation process in order to optimize the quality and structure of the obtained catalyst layer, as shown by Sharma *et al.* [204] in a study on the optimization of catalyst ink composition for the fabrication of a catalyst layer through decal transfer manufacturing.

Research on coating processes for the fabrication of catalyst layers for fuel cell electrodes seems to mainly focus on the feasibility of each coating method depending on the catalyst ink properties and components, and very few articles can be found regarding the influence of the coating process on the structural and chemical changes on the catalyst ink properties during the transition from liquid ink to solid catalyst layer. In order to investigate the transition from an ink to a solid layer, Lee *et al.* [123] analysed the structural changes within a catalyst ink upon drying. Several phenomena have been identified, such as droplet coalescence or coffee ring formation upon drying, underlining the importance of understanding this liquid-to-solid transition. Furthermore, a few studies highlight the role of hydrophilic / hydrophobic properties of both the catalyst layer components and interfaces, and the substrate [23,221,222]. In fact, it has been shown that the substrate hydrophilicity or hydrophobicity was responsible for changes in the ionomer thin film structure within the catalyst layer [221,222]. The intrinsic hydrophobicity of the gas diffusion layer and the hydrophilicity of the membrane make selecting a substrate for catalyst ink deposition non-trivial. This effect of hydrophilicity versus hydrophobicity was also studied by molecular dynamics simulation by Damasceno Borges *et al.* [221], and it was shown that the molecular rearrangement of the ionomer thin film was governed by the affinity of the substrate for water, giving rise to widely different morphologies of the ionomer thin films. For example, on hydrophilic surfaces, the ionomer was predicted to form bilayers or multilamels, whereas on hydrophobic surfaces, the ionomer preferentially formed inverted micelles or “sandwiches” with water domains.

In conclusion, it appears that the formulation of a stable, homogeneous, optimally dispersed and interactive catalyst ink is not sufficient to ensure the production of a high-quality catalyst layer, as the choice of coating method is far from being trivial. Moreover, the catalyst ink deposition step will also impact the drying step and the ink behaviour upon drying, as mentioned a few times above and discussed in more detail in the next paragraphs.

### 3.3. The drying process

Once deposited onto the substrate, unless the chosen coating process includes a solvent removal step, the catalyst ink usually goes through a drying process for solvent evaporation, resulting in the catalyst layer [23,39], as shown by **Figure 8**. The end goal of the operation is to obtain a thin homogeneous electrode, with adequate structure and properties, as discussed in section III-1 of this review. Upon solvent evaporation, numerous physical phenomena occur within the drying catalyst ink layer, such as sedimentation, shrinkage, cracking or migration [35,223–225]. These phenomena are schematized on **Figure 8** and are affected by both the drying process in itself and the catalyst ink properties [226]. They tend to generate inhomogeneities and defects within the catalyst layer, thus the drying parameters should be carefully tailored in order to better control the drying step.



**Figure 8:** Catalyst layer drying process and associated phenomena

A few drying methods are reported in the literature, which can be divided into two categories. The catalyst ink layer can either be dried through processes requiring atmospheric pressure or under vacuum conditions. At atmospheric pressure, drying processes most generally involve the use of an air flow or of heat, as is the case for oven drying and heated substrate drying [227,228]. These methods are quite similar in the sense that temperature is the driving force for solvent evaporation. In oven drying, the catalyst ink layer is placed in a temperature- and air-flow-controlled oven, typically at temperatures ranging from 50 to 120°C [227,229] depending on the solvent to be evaporated, granting a faster drying process than at ambient air drying. The efficiency of drying is in this case also favoured by the convection phenomenon. For heated substrate drying, the catalyst ink layer is placed on top of a heating plate instead of in an oven. With these two methods, temperature control allows for tuning of the evaporation rate, but overheating may also occur, as explained further down in this section.

Drying methods utilizing vacuum conditions accomplish solvent removal by using and adjusting other parameters than temperature, thus withdrawing from the potential consequences of heat on the catalyst ink system. Two drying methods are commonly found in this category, namely freeze drying and vacuum drying [35,49,228,230]. Freeze drying consists of three steps [230]. The to-be-dried catalyst ink layer is first frozen to ensure the preservation of ionomer and catalyst network structure and the creation of solvent crystals. The freezing step needs to be rapid and able to bring the catalyst ink layer below its triple point to avoid ice crystal formation and ensure sublimation rather than melting

in the subsequent step. Vacuum pressure is then applied to the frozen layer, which generates solvent sublimation. After sublimation, the temperature is then risen to allow evaporation of residual solvent moisture. In vacuum drying, the catalyst ink layer is placed directly into a vacuum chamber, where vacuum pressure is applied, thus lowering the solvent boiling point [229]. Boiling temperature is then either attained spontaneously or with the use of heat, solvent vapours are then generated and continuously removed from the chamber, until the catalyst layer is dried. The chamber is finally depressurized to atmospheric pressure.

Although oven and heated substrate drying are simpler and more cost-effective methods for drying the catalyst ink layer, studies on drying processes suggest that freeze drying leads to improved catalyst layer properties. In fact, in comparative papers on drying methods for catalyst layers, both Liu *et al.* [35] and Talukdar *et al.* [229] report that freeze drying improves the porosity and the electrochemically active surface area of the catalyst layer, which helps minimize mass-transport loss during PEMFC operation. This effect is due to the freezing step preserving the cohesive ionomer and catalyst network within the ink, preventing the layer from collapsing under solvent vaporization. This was also reported by Pan *et al.* [49] who concluded on the better preservation of the ionomer dispersion state upon freeze-drying as opposed to other drying methods, and the subsequent boost in cell performance.

The porosity created after solvent removal is often regarded as a critical parameter in the assessment of the quality of a catalyst layer since it is accounted for mass transport and water management, as explained in the first part of this section [39,226,228,231]. This consideration was confirmed through numerical simulation in several studies. For example, Abraham and Murugavel [43] studied the effect of catalyst layer porosity on cell performance. It was found through a numerical method of mesh generation that catalyst layer porosity could be optimized to improve the cell water content and overall current density. This conclusion was also reached in a different numerical simulation study by Sabharwal and Secanell [232], who furthermore observed that an optimized porosity could reduce water accumulation, promote water transport and prevent water breakthrough into undesirable cell areas. However, in a study on the formation of the porous structure within catalyst layers, Suzuki *et al.* [223] give a more nuanced point of view, arguing that pore size is the leading factor over porosity when it comes to the effect on cell performance. This slightly differing conclusion could point towards the catalyst layer morphology sensitivity to manufacturing process - and particularly to coating process, as seen in the previous section of this chapter - since the catalyst layers were all prepared in this study via decal transfer followed by hot pressing.

Upon drying, solvent intrinsic properties and interactions with other catalyst ink components play a major role in the behaviour of the catalyst ink layer [233], especially in processes where the solvent is evaporated rather than vaporized as is the case of drying at atmospheric-pressure and of vacuum drying. In fact, not only does solvent evaporation influence the final porosity of the catalyst layer, but it also affects the overall morphology and microstructure of the catalyst layer [26,223]. Upon drying, the solid content is progressively increased until the catalyst layer is dried. This evaporation has been established to occur in two steps, the first one being sedimentation of the solid content up to a solvent saturated catalyst layer, the second step being shrinkage of the saturated catalyst layer by evaporation of the residual solvent and creation of the catalyst layer porosity [223,225].

Sedimentation and shrinkage steps are influenced by the evaporation rate of the solvent, which is governed by two sets of factors during the drying step [225,226,233]. On the one hand, technical drying parameters, such as temperature, relative humidity and pressure, are at play. They influence the advancing solidification front of ionomers occurring at the ink / atmosphere interface and dictate the potential aggregate formation in the catalyst layer. In a study on the effect of drying temperature on the catalyst layer structure, Yang *et al.* [226] observed that the higher the drying temperature the more

aggregated the final structure of the catalyst layer. More precisely, while the size of primary particles remained constant, secondary aggregates became gradually larger with increase of the drying temperature, resulting in a looser structure with more pits. This observation could be due to a collapsing effect of a more brutal ink-to-solid catalyst layer transition due to faster solvent evaporation at higher temperatures, where the weak electrostatic interactions sustaining the ionomer and catalyst network within the liquid ink are not allowed to persist. For the same reasons, relative humidity and solvent vapor removal are to be controlled, ensuring a smooth transition from ink to solid layer.

On the other hand, intrinsic physical properties of the solvent, such as boiling point and vapor pressure, also have an impact on the evaporation rate during the catalyst layer drying step [53,54,157,178]. In a study on the effect of dispersion medium on catalyst layer microstructure, Ren *et al.* [178] demonstrated that the water / alcohol solvent ratio impacted the resulting catalyst layer microstructure and electrochemical properties. It was overall concluded that a compromise between pore structure density and free ionomer amount could be reached through modulation of the alcohol content, which was beneficial to mass and local transport within the cell. More generally, no consensus has been reached on whether high or low boiling point solvents should be preferred. Some studies advise choosing a low boiling point solvent in order to fasten the drying process [54]. Others recommend a high boiling point solvent to ensure slower drying and prevent crack formation and inhomogeneity during solvent evaporation [53,157].

While generally regarded as defects [54,157,160,234], cracks within the catalyst layer are sometimes promoted because if well structured, they have been shown to help with water management within the operating cell [76,235]. For example, Ahn *et al.* [235] designed a catalyst-coated membrane containing guided cracks which were obtained by mechanically stretching the material. The resulting electrode and cell were shown to exhibit better performance and more efficient water transport. More often than not, cracks are considered undesirable. They can oftentimes result from a fast solvent evaporation at very high solvent content, an inadequate ionomer binding network, temperature fluctuations during the drying step, or even interactions with the substrate. Cracks are shown to form randomly along catalyst particle aggregation [157] and tend to propagate over time [234] thus lowering the electrochemically active surface area and accelerating the ageing of the cell.

Overall, changes in evaporation rate, as well as the coating method choice, induce concentration and temperature gradients within the drying ink [227,236], which affect the drying process. These phenomena promote an inhomogeneous solvent evaporation and a particle migration effect within the drying catalyst layer [237,238], accentuating inhomogeneity in solid content distribution in the catalyst layer thickness. However, there is no consensus on whether this inhomogeneity should be regarded as detrimental or beneficial to fuel cell operation. In fact, using coarse-grained molecular dynamics for an ink evaporation simulation, Guo *et al.* [236] observed that a slow evaporation allowed for a more dispersed thin ionomer film on the catalyst surface, which was favourable to the formation of a continuous ionomer network. On the other hand, ionomer particles tended to segregate more during a faster evaporation, leading to a coarser network which impaired the proton conduction capacity of the catalyst layer. In a study on roll-to-roll manufacturing, Mauger *et al.* [227] observed that catalyst layers formed after spray coating were less prone to the formation of a solidification front, whereas catalyst layers coated from thicker inks through slot-die coating exhibited an enrichment of ionomer at the surface. This ionomer concentration gradient was considered to be beneficial to the cell performance, due to the consequent creation of a low-resistance interface between the ionomer-enriched catalyst layer and the proton conducting membrane.

All in all, the technical parameters of the catalyst layer drying process are not to be disregarded, as they affect the final catalyst layer structure and properties. The choice of the drying method, while being more limited than the choice of the coating method or the catalyst ink formulation parameters, is not trivial and should be made in accordance with the overall fabrication process. A few phenomena are induced by the drying of the catalyst ink layer, such as structural rearrangements, crack formation or inhomogeneities due to concentration or temperature gradients. These phenomena can be tuned through modulation of the drying parameters and ink formulation in order to reach final catalyst layer specificities which will optimize cell operation depending on the previous fabrication steps.

## 4. Conclusions and perspectives

This review gives an overview of the PEMFC electrode fabrication process, from formulation of the catalyst ink to integration of the catalyst layer into the PEMFC stack. In the first chapter, the catalyst ink preparation process is discussed. The catalyst ink components have been at the heart of extensive research over the past few decades. Research on the ionomer focuses on achieving maximization of proton conduction capacity without impairing mechanical or chemical stability of the catalyst layer. Advances on the catalyst system are of different kinds. On the one hand, research on the traditional use of Pt-coated carbon black particles focuses on improving catalyst utilization in order to reduce costs. On the other hand, novel catalyst systems are emerging, including Pt-free and shape-controlled catalysts. Progress on the solvent focuses on understanding ionomer / solvent / catalyst interactions and is not to be disregarded, as the solvent acts as a crucial intermediary, bridging the behaviour of catalyst ink at the microscopic level with its macroscopic behaviour during deposition and drying. Mentions of additives as protective, performance enhancers or physical integrity and durability improvers are also made. Overall, research on the catalyst ink components progresses towards an integrative perspective. Concerning the ink formulation methods, while their main role is to ensure homogeneity and stability of the catalyst ink, the main challenge is to control ink properties, especially flow behaviour, which remains crucial for the subsequent deposition of the ink.

In the second chapter, the catalyst layer preparation process is considered. Specifications on targeted catalyst layer properties are of multi-scale dimensions. First, macro- and microscopic structural properties are required, such as porosity, thickness or three-phase interface structure. These structural requirements in turn ensure the transport properties of the catalyst layer, which also are multi-dimensional. These specifications are not only achieved through the choice of primary ionomer, catalyst and solvent components, with the help of additives and numerical modelling, but they are also influenced by the catalyst ink coating and drying processes. In fact, numerous coating and drying methods can be employed. The physicochemical properties of the catalyst ink, such as rheological behaviour or solvent vapor pressure, usually orient the choice of coating and drying process. However, the reciprocal situation is also often described, where the catalyst ink formulation parameters are retrospectively adapted to the coating and drying processes specifications to improve the catalyst layer properties.

Overall, the fabrication of PEMFC electrodes is a well-established process, including various choices of components for catalyst ink formulation and numerous techniques for dispersion, deposition and drying of the catalyst ink slurry, which enable tailoring of solutions to ensure best processability. However, the catalyst ink is a complex multi-component system. Decades of research have been paving the way for understanding the links between properties, structures and performance within the catalyst inks and their subsequent catalyst layers, improving the overall PEMFCs competitiveness.

Another crucial aspect of PEMFC electrode fabrication to be kept in mind is the consideration of *in situ* implications for catalyst layers, such as ageing or degradation upon operation of the cell. The fuel cell operating conditions are usually aggressive, whether it be chemically, electrically or thermally speaking [16,51,173]. Thus, fuel cell components are subject to ageing and degradation. All the more so since PEMFC electrochemical and mechanical phenomena are coupled and interdependent. In fact, it is stated that the main challenge is to maintain mechanical stability while ensuring the reduction of transport resistance in order to improve both durability and performance of the fuel cell, as explained by Kusoglu and Weber [174]. PEMFC degradation and stability is a vast field of research and numerous methods have been developed to study and tackle the ageing of fuel cells [56,175,239–243]. Assessment and monitoring of parameters and phenomena such as flux distribution, water management, gas crossover, corrosion, thermal and mechanical stability give some precious feedback to readjust catalyst ink formulation and processing parameters.

All in all, despite significant advancement in all fields concerning preparation and processing of catalyst inks for the fabrication of PEMFC electrodes, crucial challenges remain in enhancing performance and reducing costs. Addressing these challenges requires a multidisciplinary perspective. More essentially, it also requires an integrative approach, as the interplays between preparation and processing hold the key to unlocking the potential of PEMFCs.

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