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An overview of the uses of polymers with intrinsic microporosity as binders for electrocatalysis

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ABSTRACT

This comprehensive review provides a detailed analysis of the potential of polymers with intrinsic microporosity (PIMs) as specialized binders for electrochemical applications. The quest for improved fuel cell and electrolyzer performance has driven extensive research on binders. Early investigations focused on conventional binders, aiming to enhance mechanical properties and adhesion. However, limitations in mass transport prompted the search for novel materials with superior gas permeability, driving interest in PIMs. Analyzing recent advancements and insights presented in the literature, we elucidate the distinct advantages offered by PIMs, such as chemical stability and enhanced gas permeability. The latter attribute is crucial for a binder in electrochemical devices, allowing efficient transport of reactants (e.g., hydrogen, oxygen) to active sites within the catalyst layers, significantly improving device efficiency and reaction rates. By synthesizing and assessing key research findings, this review aims to pave the way for future advancements in PIM-based binders for electrochemical applications, filling a notable gap in the existing literature.

1. Introduction

In recent years, the growing demand for sustainable energy conversion and storage technologies has significantly increased interest in electrochemical systems such as fuel cells, water electrolyzers, and CO_2 electrolyzers[1]. Fuel cells convert the chemical energy of fuels, typically hydrogen, directly into electricity with high efficiency and low emissions[2]. Water electrolyzers, in contrast, use electrical energy to split water into hydrogen and oxygen, enabling the production of green hydrogen from renewable sources[3,4]. CO_2 electrolyzers further expand this concept by electrochemically converting carbon dioxide into value-added chemicals and fuels, offering a potential pathway for carbon utilization and emission reduction[5].

A key component common to these electrochemical devices is the Membrane Electrode Assembly (MEA). A MEA is a layered architecture designed to maximize electrochemical reactions while minimizing transport losses [6]. Ionomers play a fundamental role in MEAs, as they are present in multiple components of the assembly, where they adopt different morphologies and consequently perform distinct functions[7]. Importantly, a catalyst-layer binder does not have to be an ionomer. Non-ionic binders such as PTFE, PVDF and other polymers are widely used when the electrolyte or membrane supplies ionic contact through a different pathway[8]. We here refer to ionomeric binder because this review specifically addresses binder architectures in which the polymer simultaneously provides cohesion and local ionic transport that are of particular relevance for proton exchange membrane fuel cells (PEMFCs), Anion Exchange Membrane Fuel Cells (AEMFCs) and electrolyzer catalyst layers.

Indeed, an MEA is generally composed of three main elements:

1. The Ion Exchange Membrane (IEM), which is made up of ionomers serving as a continuous, dense phase, responsible for i) the physical separation of reactants (fuels), ii) the electronic insulation and iii) the selective transport of ions[9,10]. The type of ion transported depends on the device configuration: Proton Exchange Membranes (PEMs), used in Proton Exchange Membrane Fuel Cells PEMFCs and

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Proton Exchange Membrane Water Electrolyzers (PEMWEs), conduct H^+ ions[11–13]. On the other side, Anion Exchange Membranes (AEMs), used in AAEMFCs and Anion Exchange Membrane Water Electrolyzers (AAEMWEs), conduct OH^- ions[14–16].

2. The Catalyst Layers (CLs), which are coated on each side of the IEM. The CLs are composed of i) a catalyst (Pt, IrO_2, Ni, Ag, Cu, etc.) [17–21], ii) a support material (optional, *e.g.* carbon or oxides) and iii) an ionomeric binder. In contrast to IEM, the ionomers presented here as binders are a dispersed phase that provides local ionic conduction, ensures mechanical adhesion and defines reactive interfaces [7].
3. The Gas Diffusion Layers (GDLs) or Porous Transport Layers (PTLs). These layers simultaneously distribute gases or liquids, remove reaction products and provide electronic conduction[22]. GDLs are not strictly part of the MEA but they are essential for device operation.

Thus, the MEA is a fundamental component, which influences the overall performance of the electrochemical device in terms of ohmic resistance, mass transport losses, mechanical and chemical stability and water transport and distribution[23]. Since ionomers are present under different shapes in two components of the MEA, the deep study of their chemistry, distribution and content are pivotal for the overall performance of the device. Fig. 1 shows a schematic representation of the MEA, whereas Table 1 provides a summary of the location, morphological scale, role, and the most widely adopted technologies of ionomers within the MEA.

This review will focus specifically on ionomeric binders in the catalyst layers. Before discussing the specific characteristics that ionomeric binders must possess, it is essential to introduce the different types of electrochemical reactions that occur in PEMFCs, water electrolyzers, and CO_2 electrolyzers. In PEMFCs, Hydrogen Oxidation Reaction (HOR) and Oxygen Reduction Reaction (ORR) occur at the anode and cathode respectively[24]. In water electrolyzers, Oxygen Evolution Reaction (OER) and Hydrogen Evolution Reaction (HER) occur at the anode and cathode respectively[25,26]. Considering CO_2 electrolyzers, OER and CO_2 Reduction Reaction (CO_2RR) occur at the anode and cathode respectively[27,28]. Table 2 summarizes these reactions in relation to the adopted electrochemical device.

Such electrochemical reactions occur only within the CLs of MEAs, more precisely in a region known as triple-phase boundary (TPB), where the catalyst, the ionomers and the reactants coexist simultaneously[29].

Table 1
Schematic summary of the location, morphological scale and role of ionomers within the MEA.

Location	Morphological Scale	Role
IEM	Macroscopic	Ionic conduction
CL	Nanometric	Binding action
		Local ionic conduction
		Interface engineering (e.g. wettability, porosity)
		Electron conduction

Table 2
Summary of electrochemical half reaction occurring at the anode and cathode in fuel cell, and water electrolyzers and CO_2 electrolyzers.

Electrochemical device	Anode reaction	Cathode reaction
Proton Exchange Membrane Fuel Cell	Hydrogen Oxidation Reaction $H_2 \rightarrow 2H^+ + 2e^-$	Oxygen Reduction Reaction $½\ O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Anion Exchange Membrane Fuel Cell	Hydrogen Oxidation Reaction $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	Oxygen Reduction Reaction $½\ O_2 + 2H_2O + 2e^- \rightarrow 2OH^-$
Proton Exchange Membrane Water Electrolyzer	Oxygen Evolution Reaction $H_2O \rightarrow 2H^+ + ½\ O_2 + 2e^-$	Hydrogen Evolution Reaction $2H^+ + 2e^- \rightarrow H_2$
Anion Exchange Membrane Water Electrolyzer	Oxygen Evolution Reaction $2OH^- \rightarrow H_2O + ½\ O_2 + 2e^-$	Hydrogen Evolution Reaction $2H_2O + 2e^- \rightarrow 2OH^- + H_2$
Proton Exchange Membrane CO_2 Electrolyzers	Oxygen Evolution Reaction $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	CO_2 Reduction Reaction $xCO_2 + nH^+ + ne^- \rightarrow Cn$ product $+ zH_2O$
Anion Exchange Membrane CO_2 Electrolyzers	Oxygen Evolution Reaction $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$	CO_2 Reduction Reaction $xCO_2 + nH_2O + 2e^- \rightarrow Cn$ *product* $+ zOH^-$

In this regard, at the TPB:

1. The catalyst provides sites where reactants are adsorbed and react.
2. Ionomers hold the catalyst particles together, while simultaneously binding them to the support, enabling pathways for ion transport.

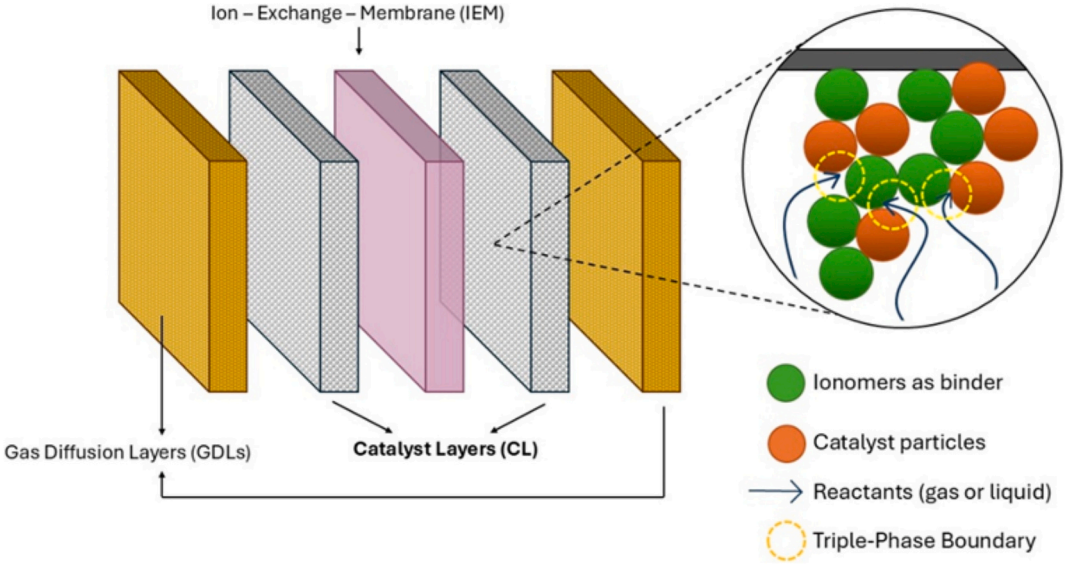


Fig. 1. Schematic representation of the Membrane Electrode Assembly (MEA), highlighting the Ion Exchange Membrane (IEM), the Catalyst Layers (CLs), and GDLs. The inset shows a zoom on the components of the CL, namely the ionomeric binder, the catalyst particles, the reactants and the triple-phase boundaries (TPB).

3. Fuels, in the form of gaseous or liquid reactants, are oxidized or reduced, depending on the species involved and the place in the device.

CL performance is governed by the simultaneous percolation of electronic, ionic, and molecular transport pathways. The triple-phase boundary (TPB) is therefore more rigorously understood as a region where at least three transport functions overlap: (i) electronic conduction through the electrically connected catalyst and/or support network, (ii) ionic conduction through the ionomer or electrolyte, and (iii) mass transport through the pore and ionomer phases[29]. The ionomer does not contribute to the electronic current because electrons generated or consumed at catalyst sites move through the electrically percolating catalyst/support phase to the GDL and external circuit. This distinction is particularly important when assessing PIM binders, because increasing binder loading can improve ionic connectivity while simultaneously interrupting electronic particle-to-particle contacts and increasing local transport resistance. Furthermore, TPB failed to describe modern porous catalyst layers in which the electrochemically active region is spatially distributed over catalyst, ionomer, liquid and gas domains[30]. Electrons must be allowed to percolate from the catalyst nanoparticles through the electronically conductive catalyst/support network toward the current collector while ions should be able to migrate through the ionomeric phase and both reagent and products must passing through the hierarchical pore network and the ionomer film itself[31]. Consequently, a catalyst particle generally contribute to the measured electrochemical current only when these transport pathways overlap over a characteristic reaction–diffusion length scale[32].

In this context, the ionomer plays a crucial role, controlling the access of reactants to the catalytic sites, and thus governing the extent and effectiveness of the TPB. A scarce amount of ionomers can leave catalytic sites ionically isolated, reducing the electrochemically active surface area, whereas an excessive quantity can block pores and hinder reactant transport. This delicate balance underlies the need for a trade-off between ionic conductivity and mass transport in MEAs[33]. For the sake of completeness, it is worth emphasizing that factors other than ionomers also modulate the formation and stability of the TPB, such as catalyst particle size and dispersion, porosity, tortuosity of the layer, and operational conditions such as humidity and temperature[34].

Perfluorosulfonic acid (PFSA) ionomer is the most widely used binder technology in electrodes for fuel cells and electrolyzers [7,35–37]. In recent years, interest in alternative ionomers has increased significantly, driven both by the need to further improve electrode performance and by growing regulatory and environmental concerns associated with fluorinated materials[38,39]. Among PFSA ionomers, Nafion® has been the benchmark material since its invention in the late 1960s, owing to its well-characterized structure and performance [40–42].Nafion® is therefore treated throughout this review as the principal benchmark rather than as a material to be excluded from the discussion. Its long-standing use, well-characterized proton conductivity, and catalyst-layer behavior provide the reference against which hydrocarbon, fluorine-lean and fluorine-free PIM-based binders should be evaluated. Nevertheless, scientific research is moving toward technologies that avoid the use of fluorinated compounds, as their manufacture requires hazardous and potentially environmentally harmful chemical feedstocks, contributing to their relatively high cost. In addition, PFSAs show also other drawbacks like the high gas permeability and the limited stability at elevated temperatures[43,44]

A growing number of studies have focused on fluorine-free hydrocarbon ionomers, among which Polymers with Intrinsic Microporosity (PIMs) emerge as promising candidates[45]. No review on this topic has yet been published in the literature; therefore, this work aims to provide an overview of PIM-based ionomers in fuel cells and electrolyzers, highlighting their advantageous characteristics and discussing their future prospects. Beyond describing PIM-based ionomers, this work frames them within the broader landscape of ionomeric binders used in fuel cells and electrolyzers. Current binder technologies are reviewed, and the key physicochemical properties required for their effective implementation are discussed.

2. The role of ionomers as binders in electrochemical devices

Research over the last three decades has identified PFSA ionomers as the material of choice in MEAs, serving both as continuous polymer matrix in the IEM and as dispersed ionomers within the CLs, thanks to their distinctive chemical structure and resulting physicochemical properties. Considering both the IEM and the CL, the perfluorinated backbone of PFSA provides exceptional chemical and electrochemical stability under the harsh oxidative and acidic conditions typical of PEFCs and electrolyzers, while the sulfonic acid side chains ensure high proton conductivity when adequately hydrated. This combination enables PFSA ionomers to simultaneously maintain mechanical integrity and efficient ionic transport over extended operating times [46] (Fig. 2).

The comparison between fluorinated and fluorine-free ionomers should not, however, be interpreted as a binary choice. Fluorinated chemistry can provide valuable oxidative stability, hydrophobicity and controlled water management, whereas hydrocarbon backbones can reduce fluorinated-material burden and offer additional structural tunability. Recent fluorine-lean phosphonated PIMs illustrate an intermediate strategy in which a limited amount of fluorine is retained while a rigid, highly kinked backbone provides high oxygen transport and phosphonic-acid groups provide proton conduction. Such hybrid designs are better described as a continuum of chemical strategies rather than a simple fluorinated versus fluorine-free dichotomy[47].

In the CL, the amphiphilic nature of PFSA ionomers allows them to adapt to the complex, high-surface-area morphology of carbon-supported catalyst particles, forming thin ionomer films that establish continuous proton-conducting pathways to active sites [48]. The strong acidity of the sulfonic groups promotes effective proton exchange at the catalyst–ionomer interface, while the fluorinated backbone limits excessive swelling and dissolution, preserving the structural stability of the electrode[35]. At the same time, the phase-separated morphology of PFSA ionomers, consisting of hydrophobic fluorinated backbones and hydrophilic sulfonic acid domains, strongly influences local water content, gas transport, and interfacial properties within the CL[48]. These attributes allow PFSA ionomers to fulfill a dual function within the MEA, acting as a robust solid electrolyte in the membrane and as a multifunctional binder, proton conductor, and interfacial modifier in the catalyst layer, thereby underpinning the formation of stable and efficient TPB and contributing decisively to overall device performance [49].

As alternatives to PFSA ionomers, hydrocarbon-based proton exchange ionomers have been extensively explored owing to their lower cost, tunable chemical structures, and reduced environmental impact [50].

Compared to PEMs, AEM-based systems require fundamentally different structures, in terms of ionomer chemistry and catalysts. The primary and most significant difference is that AEM selectively conducts negatively charged hydroxide ions OH^-, meaning that the polymer matrix must display positively charged groups on the side chain[14]. As in the case of PEMs, the ionomers forming the IEM and the ionomers present in the CL are largely based on the same material, but with molecular weight, degree of functionalization, and solubility optimized for the specific application. The second difference is that AEM can also use cost-effective non–noble metal catalysts such as nickel, cobalt, copper and iron, in contrast to the expensive platinum- and iridium-based catalysts used in PEMFCs and PEMWEs[51–54].

These aspects make AEM-based technologies highly attractive for the market; however, they are still at an early stage of development and face several challenges, such as degradation of the polymer matrix upon exposure to hydroxide ions in an alkaline environment[55,56]. Taken together, ionomers for AEMs must exhibit high OH^- conductivity,

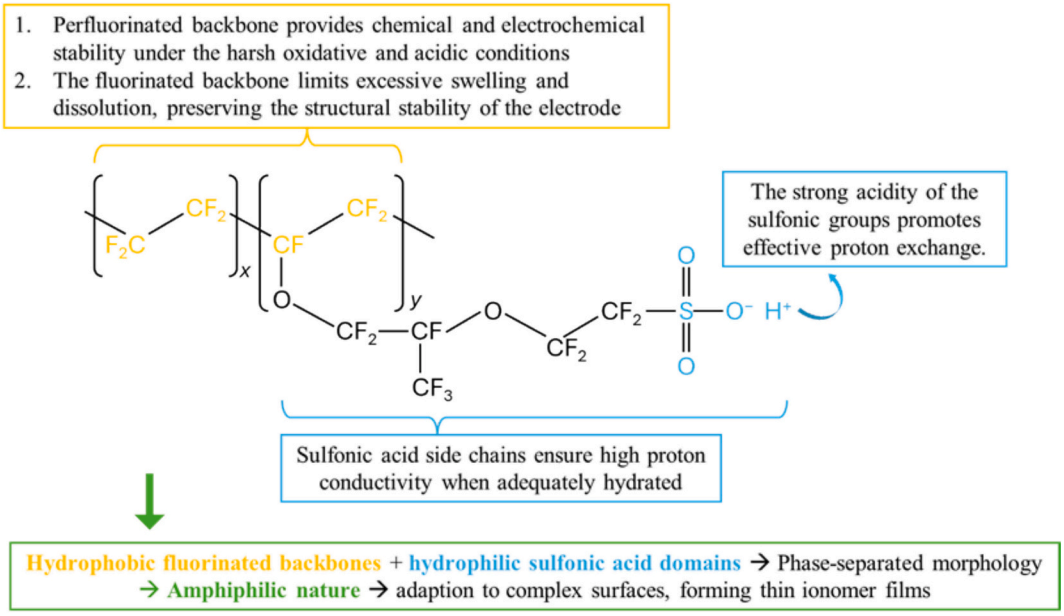


Fig. 2. Schematic representation of the structure of Nafion® widely used as ionomeric binder in PEMs, highlighting the roles of each chemical group[40–42].

excellent alkaline stability, controlled water uptake and swelling behavior, appropriate hydrophobicity, efficient cation–hydroxide–-water co-adsorption, and stable local pH conditions[34]. In this regard, a wide variety of polymer backbones and cationic groups have been extensively investigated over the past decades. Polymer backbones containing aromatic ether linkages and electron-withdrawing groups have been shown to be particularly vulnerable under alkaline conditions. Therefore, this class of polymers should be avoided, even though it involves unfortunately many inexpensive and readily available materials, such as poly(phenylene ether ketone) (PEEK), poly(ether sulfone) PESU, and poly(phenylene oxide) (PPO). Indeed, nowadays within academic research, PPO remains the most extensively studied polymer, typically functionalized with quaternary ammonium, imidazolium, or piperidinium groups[57]. Other polymer matrixes were investigated including polyethylene, polybenzimidazole and polystyrene, whereas imidazolium, piperidinium and quaternary ammonium groups were conceived as cationic moieties for OH^- transport[58]. From a commercial perspective, Sustainion® and PiperION® are the most widely used AEM technologies. Sustainion®, developed by Dioxide Materials, has been extensively employed both as a membrane and as an ionomer in catalyst layers for AEM fuel cells, water electrolyzers and CO_2 electrolyzers. Its aromatic polymer backbone and quaternary ammonium functional groups provide high OH^- conductivity and low area-specific resistance, enabling high current densities under alkaline conditions. Sustainion® membranes are available in various thicknesses and configurations, tailored for specific applications, including CO_2 electrolysis and water splitting. PiperION®, produced by Versogen, is based on a rigid aromatic backbone functionalized with piperidinium cations. It offers excellent chemical stability under alkaline conditions, while maintaining high OH^- conductivity. Both Sustainion® and PiperION® have demonstrated competitive performance in AEM devices[59–61] as shown in Fig. 3.

Among hydrocarbon-based ionomers, PIMs have recently emerged as a promising class of materials for both PEMs and AEMs. PIMs are characterized by rigid and contorted polymer backbones that prevent efficient chain packing, resulting in a network with intrinsic micropores that can facilitate mass transport while maintaining structural stability. Their structure, properties, and potential as ionomeric binders will be discussed in detail in the following sections.

2.1. Key properties of ionomeric binders

Within the catalyst layer, the ionomeric binder plays a multifaceted role that extends well beyond mechanical cohesion, directly affecting mass transport (reaction gases, ions, and water) and kinetic phenomena. Moreover, the proximity of ionomers to the catalytic sites, where operating conditions can be harsh, requires them to exhibit high chemical and mechanical stability[62]. Mass transport is typically one of the first aspects to be considered due to its dependence on multiple elements and its strong impact on device performance, particularly at high current densities, where mass transport limitations are most pronounced. Gaseous reactants, such as hydrogen (H_2) and oxygen (O_2), must permeate through the ionomer films and reach the catalyst active sites, where electrochemical reactions take place. At the same time, ions generated at these sites must be efficiently transported through the ionomer phase to the opposite electrode to complete the internal ionic circuit, while the electrons produced are conveyed through the external circuit. In PEMFCs, protons H^+ are generated at the anode and transported toward the cathode, whereas in AAEMFCs, hydroxide ions OH^- migrate in the opposite direction[63,64] as shown in Fig. 4. Beyond fuel gases and ions, water transport through ionomer films plays a critical role in governing the multi-physical mass transfer processes within the CL and the optimization of water transport would be highly promising for improving PEMFC performance on the practical operational level [65].

Additional properties that must be considered when evaluating the suitability of an ionomeric binder include its adhesive characteristics—namely adhesion to the catalyst particles, catalyst support, and membrane—as well as its resistance to radical-induced oxidative degradation and its pore-forming ability within the catalyst layer. In PEM-based systems, a further critical requirement is the ability of the ionomer to minimize sulfate anion adsorption, which can otherwise lead to significant performance losses and durability issues. In contrast, for AEM-based systems, three key properties must be taken into account: alkaline stability, cation–hydroxide–water co-adsorption behavior, and resistance to electrochemical oxidation of phenyl groups. All these aspects will be discussed in the following sections. A thorough understanding and targeted optimization of these properties are essential for the design of advanced ionomeric binders that enable high performance and long-term durability in fuel cells and electrolyzers.

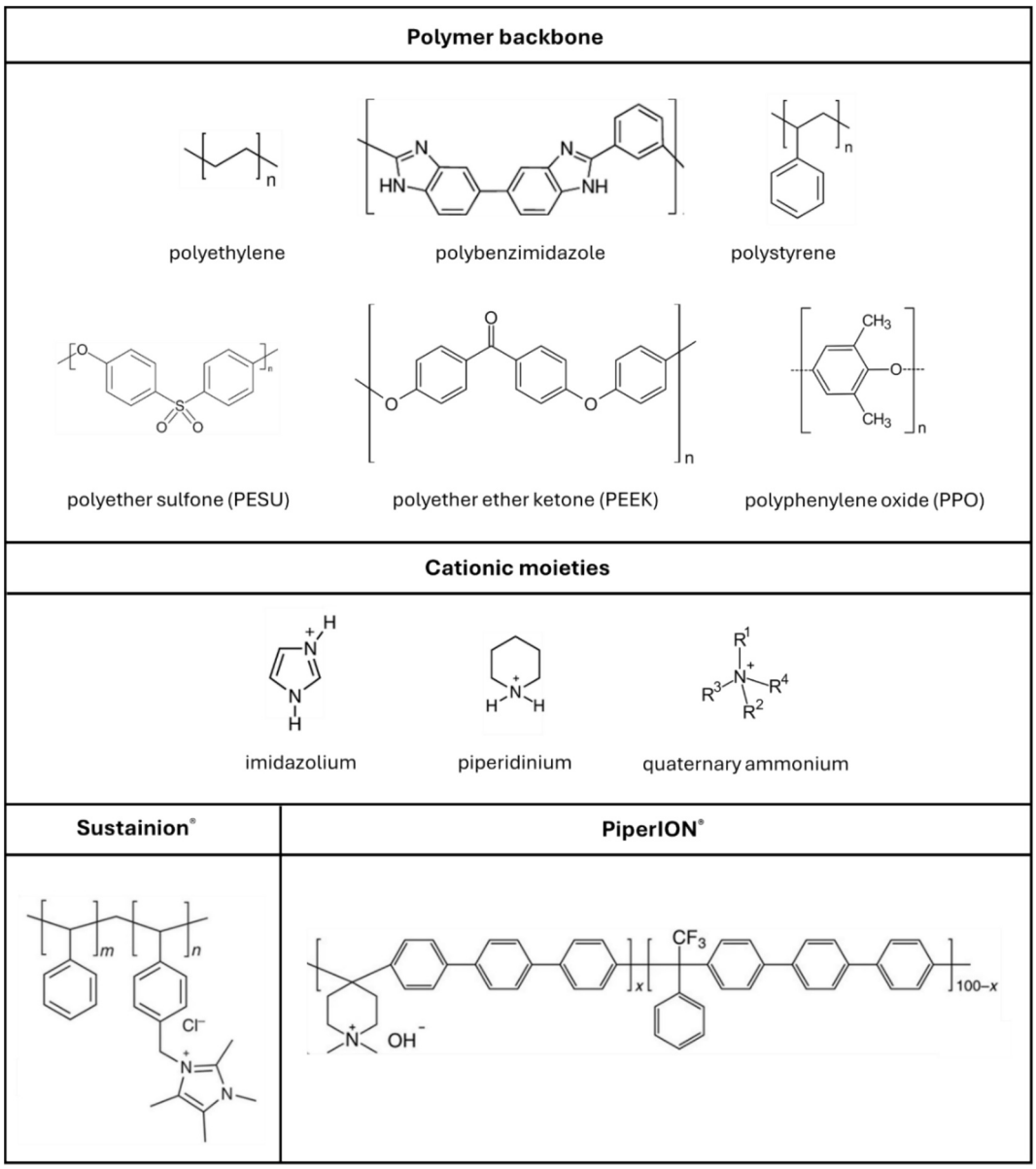


Fig. 3. Schematic structures of polymer backbones and cationic groups investigated as ionomers for AEM. Commercially available ionomers Sustainion® and PiperION® are also reported.

2.1.1. Fuel permeability

Intuitively, fuels should not permeate through the IEM, as fuel crossover leads to several detrimental effects: reduction in faradaic efficiency, voltage losses, local heat generation due to parasitic reactions, accelerated chemical and electrochemical degradation of both the catalyst and the membrane, lower performance and reduced device durability[66]. In contrast, within the CL, the ionomer must allow sufficient fuel permeability. Effective transport of reactants and removal of products through the ionomer phase are essential to ensure adequate reactant availability at the active catalyst sites, minimize mass-transport limitations, and achieve high reaction rates[67]. Therefore, an optimal design requires a clear functional distinction: the IEM must act as a strong barrier to fuel crossover, while the ionomer in the CL must provide a permeable pathway that supports efficient fuel access without compromising ionic conductivity.

Although hydrogen and oxygen permeability through the IEM can be discussed under the common framework of gas crossover, the treatment of the two gases, in terms of transport and permeability in the CL, differs significantly. Indeed, hydrogen is a small molecule, which makes it particularly prone to crossover, while its permeability in the CL is primarily governed by its high diffusivity[66]. On the other hand, oxygen is a molecule with a wider radius, and its permeability is strongly influenced by solubility and its role in oxidative degradation processes [68]. For this reason, most of the experimental and modeling work in literature focuses on oxygen transport limitations in the cathode, even though hydrogen transport phenomena within CL are also recognized as a contributor to overall transport resistance. Its gas permeation through thin ionomer films depends on ionomer distribution and nanoscale pore structure, highlighting the importance of optimizing ionomer morphology and coverage to enhance catalyst accessibility.

Oxygen permeability has long been recognized as a critical factor influencing the performance of fuel cells. Oxygen diffuses through the porous GDL to reach the CL on the cathode side. Within the CL, O_2 flow faces resistances from the diffusion within the porous architecture (bulk oxygen transport resistance, R_{bulk}) and permeation through the ionomer film (local oxygen transport resistance, R_{local}), where the last one has been confirmed to be the predominant.

A promising approach to reduce gas-transport resistance and

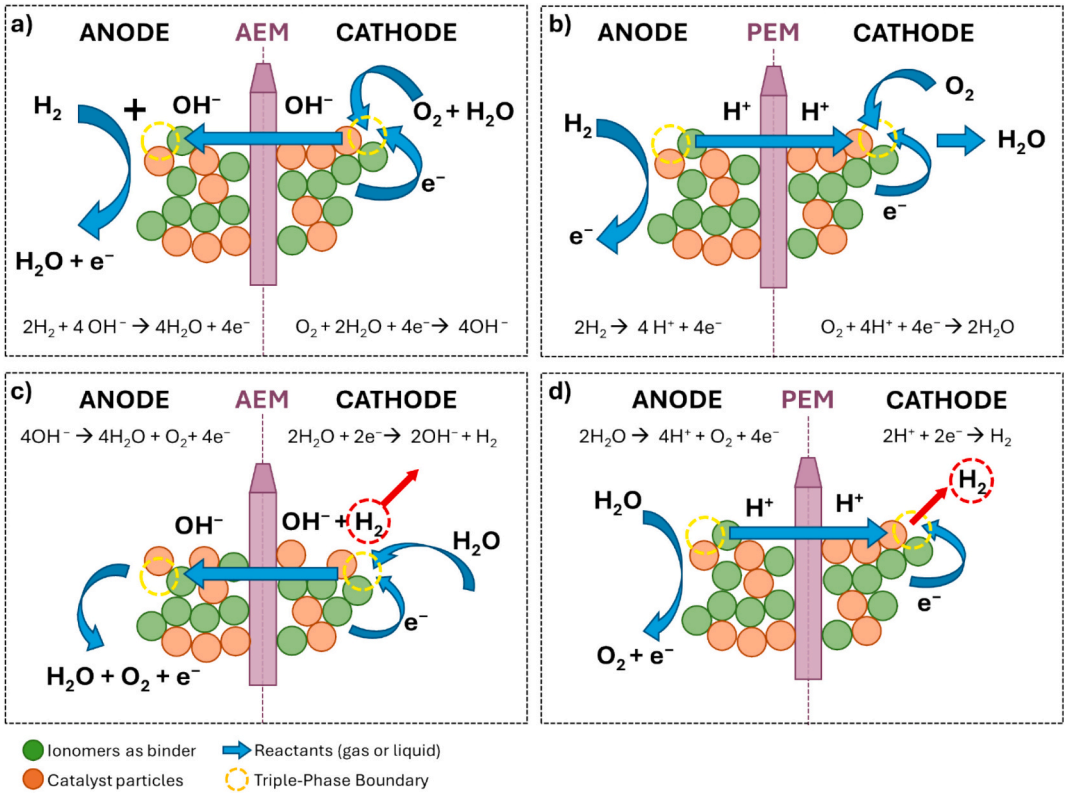


Fig. 4. Schematic representation of reactions taking place on the anode and cathode of a) AEMFC, b) PEMFC, c) AEMWE and d) PEMWE. Blue arrows highlight the directions of reactants and products. In insets c) and d) the production and release of H_2 is highlighted in red.

improve oxygen flux to electrocatalyst surfaces in the CL involves the development of ionomer binders with improved gas permeability, the so-called high oxygen-permeable ionomers (HOPIs)[69]. HOPIs can be prepared by modifying the linear backbone of conventional PFSA-based ionomers with alternative substituents or side chains[70,71]. Such additional components disrupt the matrix crystallinity, form amorphous domains and enhance the fractional free volume (FFV), which is a part of space not occupied by polymer chains, a key structural parameter controlling the diffusivity and permeability of small molecules[72]. A practical example of HOPI is the incorporation of dioxole segments or bulky ring structures in the PFSA backbone. understanding how HOPI structure influences reactant transport properties and its underlying mechanisms remains essential. Lim *et al.* investigated how different side chains can influence the transport properties of protons, oxygen and water within the CL. According to the study, a more flexible polymer structure offers advantages in water channel connectivity and proton/water diffusion. By contrast, ionomers characterized by a more rigid chain structure (i.e. with bulky ring side chains) enhance FFV formation and thus improve oxygen diffusion[73]. It is therefore noteworthy that while HOPIs positively influence oxygen permeation, they also present certain disadvantages regarding proton conduction. An analogous conclusion was elaborated by Zou *et al.* after developing a novel sulfonated aromatic polymer–based ionomer containing cyclohexyl groups. Such system exhibited high gas permeability thanks to the higher FFV in the membranes, created by the presence of the bulky cyclohexyl groups. However, the proton conductivity slightly decreased, presumably due to less interconnected/developed) ionic channels. Moreover, the addition of such hydrophobic groups reduced interpolymer entanglement and thus the mechanical properties[74].

Another important aspect concerning oxygen permeability is related to the catalyst: R_{local} increases in the case of low Pt loading[75]. By studying oxygen transport properties in ionomer films, it would be possible to tune and increase the oxygen permeability of the ionomer, and in this way the quantity of Pt at the cathode may be minimized. This would be particularly important in low-Pt-loading cathodes, where limited oxygen supply to the catalyst surface can significantly impede performance. Lowering the total amount of Pt would also lower the overall costs of the device[76].

Although CO_2 is not a fuel in the conventional thermodynamic sense, it plays an analogous functional role in CO_2 electrolyzers as the electrochemically consumed reactant. Consequently, its transport and permeability must be carefully controlled: similar to H_2 and O_2, CO_2 crossover through the IEM should be minimized, while sufficient CO_2 transport within the CL is required to sustain high reaction rates and product selectivity. In the same vein, CO_2 permeability within the CL plays a crucial role in determining mass-transport resistance, access to active sites and overall catalyst utilization. Several aspects differ significantly when considering CO_2 transport in CO_2 electrolyzers. Unlike H_2 and O_2, CO_2 exhibits lower diffusivity and limited solubility in aqueous environments, and its transport is even more influenced by local wettability, ionomer distribution, and pore architecture within the CL. As a result, CO_2 permeability is often a dominant limiting factor. These characteristics make the optimization of ionomer morphology and catalyst layer microstructure particularly critical for enabling efficient CO_2 transport[77,78].As in the discussion of H_2 and O_2 transport, similar considerations apply to CO_2. Excessive ionomer content in the CL may lead to pore occlusion, resulting in increased flooding and a reduction of available gas transport pathways. Conversely, insufficient ionomer content can cause poor ionic conductivity and limited access of reactants to the catalytic sites.

Ionomers with higher gas permeability often feature aromatic backbones which, owing to their structural rigidity, promote a higher FFV. An increased FFV enables a clearer separation between ionic channels and gas-transport pathways. Since CO_2 is transported predominantly through the gas phase, optimization of the CL porosity and tortuosity is also required. In this regard, the introduction of mesopores

and macropores with controlled size and distribution is desirable: in this way catalytic conversion primarily occurs in micropores, while meso- and macropores facilitate gas transport and diffusion.

While electrochemical devices such as fuel cells are notoriously prone to flooding, CO_2 electrolyzers are even more susceptible to this phenomenon[79,80]. In the case of CO_2 electrolzyers, flooding hinders CO_2 diffusion to the catalyst and results in an increase of the parasitic HER rate[81,82]. Consequently, particular attention must be paid to increasing local hydrophobicity: one strategy could involve the incorporation of PTFE or other hydrophobic binders within the CL.

A major challenge encountered in AEM systems (inherently alkaline systems), is carbonation, a parasitic reaction. Mitigation strategies include limiting the accumulation of OH^- near the CL and employing bipolar membranes (BPMs). A BPM consists of a cation-exchange layer and an anion-exchange layer joined together, enabling water dissociation at their interface and allowing independent control of pH at the two electrodes.

To sum up, increasing CO_2 permeability in the CL requires a careful balance between ionomer content, pore structure, and wettability. Strategies that preserve open gas pathways while maintaining sufficient ionic connectivity are essential to mitigate CO_2 transport limitations and enhance electrolyzer performance.

2.1.2. Proton conductivity

The proton transport properties, as well as the electron transport properties, are highly dependent on the bulk properties of the constituting materials, such as the FFV, the catalyst used, the amount of ionomer in the CL, and the manufacture process. Taking into account the ionomer, its architecture within the CL relies on phase segregation, creating distinct hydrophobic and hydrophilic domains with the ability to absorb water. Proton transport mainly occurs within the hydrophilic regions of these materials[83]. An important aspect is the fact that increasing the ionomer content can decrease protonic resistance, while on the other hand, it may also increase electronic resistance by reducing the number of contact points between solid particles. In addition, a higher ionomer fraction can lower the porosity of the CL, thereby hindering reactant and product transport[84]. There is therefore a need to identify an amount that represents a compromise among the characteristics listed above.

Wilson and Gottesfeld's early studies highlighted the impact of ionomer proton conductivity on PEMFC performance, demonstrating improvements by replacing non-conductive PTFE with Nafion ionomer [85]. The introduction of PFSA polymers like Nafion in the 1980s enhanced proton supply in the cathode catalyst layer, addressing a critical limitation. Over recent decades, advances in water management, oxygen supply, and membrane resistance allowed for higher current densities, re-emphasizing proton conductivity in the catalyst layer as a performance bottleneck[86].

Beyond Nafion, recent studies have explored sulfonated poly(arylene ether sulfone) (SPAES) – based systems, used both as ionomers in the catalyst layer (CL) and as membrane materials in PEMWE. These systems have demonstrated remarkable advancements compared to their Nafion-based counterparts. In particular, SPAES-based MEAs achieved a current density of 1069 mA cm^{-2} at 1.6 V, along with higher mechanical strength than the corresponding Nafion systems. Moreover, the proton conductivity of the SPAES-based system reached 112.3 mS cm^{-1} at 30 °C and 330.1 mS cm^{-1} at 90 °C, significantly exceeding the values reported for Nafion 211 (70.0 and 135.6 mS cm^{-1} at 30 °C and 90 °C, respectively). Wang *et al.* synthetized poly(sodium-p-styrene sulfonate) with absorbed MoS_2/Carbon Nanotubes (CNTs), demonstrating that the introduction of poly(sodium-p-styrene sulfonate) increased proton concentration around the catalytic sites thanks to the enriched presence of negatively charged groups, while the CNTs improved the conductivity of the electrocatalyst and prevented the agglomeration of MoS_2. Overall, this combination led to marked improvement in HER performance.

In High Temperature PEMFCs (HTPEMFCs), phosphonated or acid-doped ionomers are engineered to maintain proton conduction under low humidity while avoiding acid leaching[87–89]. Strategies include optimizing ionomer pK_a and dispersion media to tune thin-film morphology and porosity, thereby improving mass transport and stabilizing the ionomer–catalyst interface. Control of ionomer ion exchange capacity (IEC) is also critical: excessively high IEC can promote Pt dissolution and redeposition, so balanced designs are required to achieve both high oxygen permeability and long-term durability[90].

Additionally, conductive polymer additives such as poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) introduced into the ionomer phase enhanced electronic–ionic coupling within the CL, lowering cell voltage at 1 A cm^{-2} and improving long-term stability[91].

2.1.3. Water transport

The performance of electrodes in FCs depends critically on their composition, particularly the hydrophobicity and oxygen permeability of the ionomer binders. Hydrocarbon ionomers, with lower density than PFSA ionomers, have optimal loadings between 30-60%. However, PFSA-based electrodes generally outperform hydrocarbon-based ones due to their higher oxygen permeability and hydrophobicity, which mitigate flooding. Studies show that hydrophobicity correlates strongly with performance, as it prevents water-induced flooding, a key issue in such devices, especially under high current densities. The degree of hydrophobicity must be optimized to balance water management and prevent performance loss due to flooding.

As extensively reported, water management in AAEMFCs is considerably more complex than in PEMFCs. In particular, water is produced at the anode while being consumed at the cathode, which intensifies the imbalance of water distribution between the two electrodes. As a result, when the fuel cell operates at high current densities, AAEMFCs must simultaneously cope with anode flooding and cathode dehydration. An anode ionomer characterized by high water uptake and a large swelling ratio can obstruct the porous structure of the CL, thereby increasing mass transport resistance. In addition, repeated water absorption and dehydration cycles may compromise the structural integrity of the CL, leading to exfoliation and catalyst particle aggregation. On the cathode side, dehydration enhances the nucleophilicity of OH^- ions, accelerating ionomer degradation. For these reasons, ionomers combining high chemical stability with a low swelling ratio are essential to achieve high-performance AAEMFCs and ensure long-term durability[58].

2.1.4. Adhesive properties

Electrodes are characterized by a porous and brittle structure. For this reason, to develop durable MEAs, it is essential to enhance their mechanical stability and durability, by designing systems that not only reinforce and bind the electrode network, but also effectively connect catalyst particles to one another and facilitate ion transport throughout the device. In this scenario, the role of the ionomer is crucial for the adhesion between the electrode components, and the ionic conductivity between the electrode and solid polymer membrane[92]. Important factors that influence the adhesion energy of the ionomer are i) the oxidation state of the catalyst and carbon-supporting materials, ii) the hydration level and iii) mechanics. Firstly, a mildly oxidized platinum or carbon surface increases the binding energy between the hydrated thin ionomer film and the substrate. While further hydroxylation slightly strengthens this interaction, epoxidation of the catalyst or graphite surface reduces the binding energy, ultimately promoting film delamination. Regarding hydration, at high water content the Nafion® ionomer becomes more flexible and undergoes structural rearrangement on the graphite surface, leading to partial delamination. Nevertheless, the increased mobility enables the polymer chains to form bridging structures between the graphite carbon support and the Pt nanoparticles. For this reason, particularly in water electrolyzers, the presence of water must be under control. Additionally, in water electrolyzers, the oxygen-producing anode is also susceptible to catalyst detachment due to the

formation of oxygen bubbles within the 3D porous electrode[93]. The adhesion energy of the ionomer plays a key role in ensuring a stable and durable interface between the PEM and the catalyst layer (CL). Interfacial delamination between the ion exchange membrane (IEM) and the CL has frequently been reported under freeze–thaw cycling, in liquid-fuel-fed fuel cells, and during prolonged operation, particularly when conventional MEA fabrication methods provide insufficient ionomer adhesion. Such delamination can promote water accumulation at the interface and increase interfacial ionic transport resistance. Contributing stress factors include uneven compression from the bipolar plates, non-uniform electro-osmotic drag, and dimensional mismatch between the water-swollen PEM and the catalyst layer. Differences in volumetric water uptake serve as a useful predictor of interfacial instability, highlighting the need to tailor electrode composition (e.g. adjusting the ionomer/catalyst ratio or selecting appropriate binder chemistries) to improve interfacial compatibility and mechanical integrity[34].

Chen et al. [93] prepared new adhesive norbornene-based ionomers for AAEMWEs in order to improve the adhesion between the catalyst particles, the porous transport layer (PTL) and the IEM. Such molecules belong to the family of self-adherent ionomers and are based on hydroxide conducting poly(norbornene) polymers. The synthesized terpolymer ionomers have been functionalized to provide pendant sites for covalent chemical bonding of bis(phenyl)-A-diglycidyl ether to the ionomer, catalyst, and PTL. The electrodes show excellent adhesion between the catalyst particles, PTL and ionomer, as determined by adhesion measurements and electrolysis performance. The AEMWE had stable voltage performance under high current density (1 A cm^{-1} at 1.83 V with 67% voltage efficiency) for more than 600 h without degradation.

Byun et al. [92] developed an innovative technique for quantifying the mechanical robustness of electrodes in MEAs using a surface and interfacial cutting analysis system. They observed that the cohesive strength within the bulk cathode regions was nearly identical at different depths, indicating a homogeneous distribution of the ionomer binder throughout the cathode. In contrast, the adhesive strength at the cathode–membrane interface was markedly higher than the cohesive strength measured within the cathode bulk. This behavior may be explained by the lower ionomer content in the cathode compared to the membrane. As a result, intermolecular diffusion between the cathode ionomer and the membrane ionomer at the interface is more pronounced than diffusion occurring within the bulk of the cathode. This enhanced interdiffusion at the interface leads to stronger adhesive strength compared to the cohesive strength within the cathode bulk as shown in Fig. 5. XPS analysis revealed that the fluorine content of the bulk region of the cathode was essentially constant, regardless of the examination depth, whereas the fluorine content at the interface was higher than that in the bulk region, which may be attributed to the relative abundance of ionomers on the membrane surface. The adhesive strength at the cathode–membrane interface increased as the ionomer binder content in the cathode rose, and a comparable trend was also observed for the anode. This behavior is likely due to the enhanced intermolecular diffusion of ionomer binders from the electrode into the membrane at higher ionomer contents, which promotes stronger interfacial bonding and results in increased adhesive strength. Furthermore, the adhesive strength of the cathode increased with an increase in the assembly temperature rose from 100 to 140 °C, followed by a plateau at 160 °C. This behavior can be attributed to the enhanced intermolecular diffusion at the interface up to 140 °C, driven by the increased thermal energy. However, once intermolecular diffusion reached saturation around 140 °C, no further improvement in interfacial bonding occurred, leading to the observed plateau at 160 °C.

2.1.5. *Resistance to radical-induced oxidative degradation*

Another crucial property that must be investigated when discussing ionomers in the catalyst layer is their resistance to radical-induced oxidative degradation. H_2O_2 (a radical precursor) and radical species such as $^{\bullet}OH$, $^{\bullet}OOH$, are the most common species that can be generated. These species mainly originate from i) incomplete oxygen reduction (ORR) in FCs, ii) peroxide decomposition catalyzed by metal ions and iii) high anodic potentials (especially in electrolyzers). Within the catalyst layer, the ionomer is more exposed to radicals since it is in direct contact with the metallic catalysts, it has a higher specific surface area, it is thinner and less protected and lastly, it experiences strong potential and concentration gradients. This makes the catalyst layer one of the most critical regions for chemical degradation [94]. For instance, PFSA degradation in PEMFCs is primarily caused by reactive free radicals, such as hydroxyl radicals generated by hydrogen peroxide, attacking sites on PFSAs like carboxylic acid groups, ether groups, and sulfonic

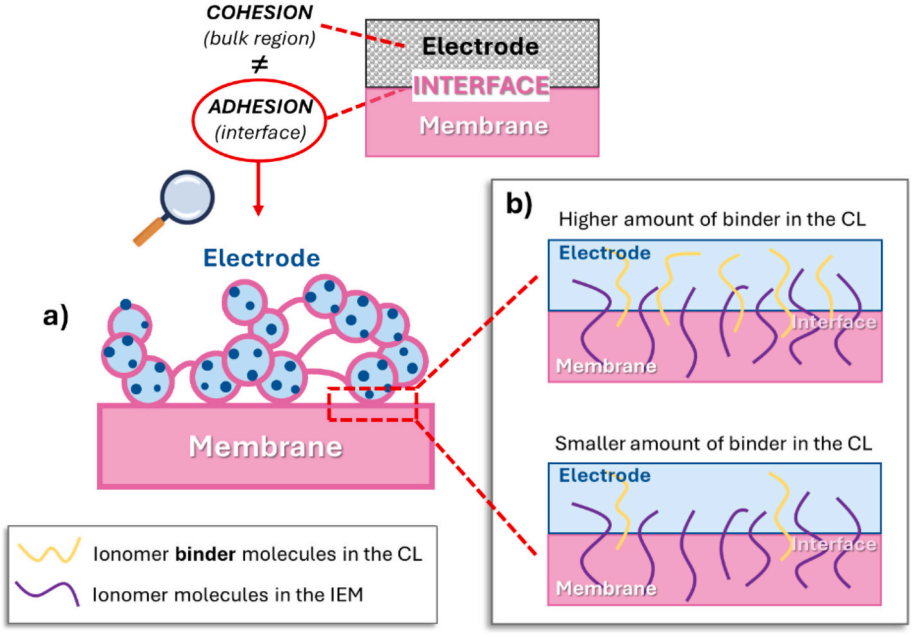


Fig. 5. Schematic illustrations of the interface a) between the electrode and the membrane in the MEA and b) the intermolecular diffusion between ionomers at the interface.

acid bonds. These attacks fragment polymer chains, reducing the mechanical and ion-exchange properties of the ionomer, which in turn decreases device durability. Radical scavengers, particularly CeO_2, are commonly used to mitigate this degradation. which rapidly degrade peroxides into oxygen and water although their effectiveness in hydrocarbon-based membranes requires further study, as degradation pathways may differ under various test conditions [95].

Because alkaline stability has been the main focus of researchers so far, it has not yet been thoroughly investigated to what extent AEMs are affected by reactive oxygen species. However, it is known that peroxides decompose rapidly upon contact with NaOH, and it is therefore possible that AEMs are relatively protected against peroxide-induced degradation due to the high pH in AEM water electrolyzers [96,97]. In addition, hydroxyl and hydroperoxyl radicals are not formed under alkaline conditions. However, in AEM-based fuel cells, the formation of superoxide radicals ($O_2^{\bullet-}$) has recently been reported. Apparently, the reduction of oxygen in the presence of hydroxide ions, leading to the formation of superoxide anion radicals and hydroxyl radicals, is catalyzed by quaternary ammonium groups[98,99]. Investigating the stability of AEMs toward superoxide radicals and identifying strategies to mitigate their effects may become an important issue in the future.

2.1.6. Alkaline stability in AEM- based systems

For alkaline anion exchange membrane fuel cells (AAEMFCs) and water electrolyzers (AAEMWEs), binders must exhibit high alkaline stability to withstand the harsh environment and maintain their structural integrity and functionality. Degradation of the functional group does not necessarily affect the mechanical integrity of the membrane but reduces the ion conductivity. In AEM, quaternary ammonium ions degrade due to nucleophilic substitution reactions, in which hydroxide ions react either with a methyl group to methanol or with a methylene group to free trimethyl amine and a polymer bound alcohol group[100]. In addition to the widely used benzyl trimethylammonium (BTM) groups, which are attached to aromatic polymer backbones through a methylene group, several other cationic groups have been explored, including imidazolium, methyl-trimethylamine, and phosphonium. Among these, imidazolium is particularly interesting because it can be functionalized at all five positions of the ring. This enables steric protection of the labile C2 position against attack by hydroxide ions and allows tuning of the electron density at C2, leading to significantly different alkaline stabilities depending on the imidazolium structure [101].

A study using model compounds showed that BTM exhibits lower alkaline stability than methyl-trimethylamine (TMA). This reduced stability is attributed to the negative inductive effect of the phenyl substituent, which increases the positive charge on the BTM group. These findings suggest that ammonium groups tethered by longer alkyl chains may be more stable than BTM. However, ethyl-TMA shows very low stability because its β-hydrogen atoms are susceptible to Hofmann elimination. Interestingly, extending the alkyl chain by one additional methylene group (propyl-TMA) improves alkaline stability, which then remains relatively constant up to hexyl-TMA before decreasing again. The enhanced stability of alkyl-TMA species with chain lengths greater than ethyl is explained by restricted free rotation of the β-hydrogen-containing group due to the additional methyl group. This conformational constraint slows down Hofmann elimination, which requires an anti-periplanar arrangement between the ammonium group and the β-hydrogen[102]. Certain phosphonium groups have demonstrated promising properties, particularly when the phosphorus atom is substituted with bulky, electron-rich groups such as trimethoxyphenyl [103]. However, the relatively high molecular weight of these systems can limit the achievable IEC. In the case of AEMs, factors such as functional group density and the rigidity of the polymer backbone are also likely to influence stability.

2.2. Other key properties of a binder

In addition to the aforementioned properties, several other characteristics are crucial for the performance and durability of electrochemical devices like fuel cells and electrolyzers, namely:

2.2.1. Pore-forming ability

The pore architecture in the electrode structure significantly impacts gas diffusion and water management, especially in high-performance operations[104]. The pore-forming ability of an ionomer refers to its capacity to generate and stabilize a hierarchical pore structure within the CL during ink preparation and drying. This property arises from the interplay between ionomer chemistry (backbone rigidity, side-chain length, ionic group density), solvent composition, and interactions with catalyst particles. In PFSA-based ionomers, phase separation between the hydrophobic fluorocarbon backbone and hydrophilic sulfonic acid domains leads to the formation of nanoscale ionic channels, while mesoscale porosity develops as the solvent evaporates and the ionomer redistributes around agglomerated catalyst particles. Pioneering morphological studies have shown how ionomer content and dispersion state control CL porosity and oxygen transport resistance in PEMFC electrodes[75,105]. Excessive ionomer loading can fill interparticle voids, reducing gas permeability and increasing mass-transport losses, whereas insufficient ionomer leads to poor ionic connectivity. More recently, advanced studies have highlighted that ionomer distribution at the nanoscale determines not only proton/hydroxide transport but also the effective pore size distribution and tortuosity[106]. In AAEMFCs, the situation is further complicated by the typically higher swelling and stronger specific adsorption of cationic ionomers, which can partially block pores or create dense interfacial films on catalyst surfaces, and this aspect will be discussed in the successive paragraphs.

2.2.2. Sulfate anion adsorption and nanoparticle dissolution

Binders must minimize sulfate anion adsorption, which can lead to nanoparticle dissolution in catalyst layers, compromising catalytic activity and durability. Sulfate anion adsorption is a well-known surface-specific phenomenon on noble metals, especially Pt and its alloys. In acidic environments containing sulfuric acid or residual sulfate impurities, sulfate and bisulfate specifically adsorb on Pt surfaces, blocking active sites and modifying the double-layer structure. Electrochemical studies demonstrated that sulfate adsorption suppresses ORR kinetics [107,108]. When sulfonated ionomers are present, the sulfonate groups can behave analogously, forming interfacial layers that alter catalytic activity and local pH. Beyond kinetic effects, sulfate or sulfonate adsorption can influence nanoparticle stability. Strongly adsorbing anions modify surface oxidation behavior and can enhance metal dissolution under potential cycling by stabilizing soluble metal–anion complexes. Studies on Pt dissolution under fuel cell-relevant conditions have shown that the presence of specifically adsorbing anions accelerates Pt oxidation–reduction transitions, which are closely linked to transient dissolution[109]. In CL containing sulfonated ionomers, local enrichment of sulfonate groups near the nanoparticle surface may therefore promote dissolution or redeposition phenomena. Furthermore, leached sulfate impurities from membrane or ionomer degradation have been implicated in additional site blocking and corrosion processes [110].

2.2.3. Adsorption of the ionomer components in AEMFC anodes

In the early stages of AAEMFCs development, the main challenges were the low hydroxide conductivity and limited chemical stability of AEM. The introduction of highly conductive and chemically stable AEMs, together with soluble ionomer dispersions in the early 2010s, enabled the fabrication of functional MEAs. Nevertheless, the initial cell performance remained modest, likely due to the sluggish HOR kinetics in alkaline media. Consequently, research efforts shifted toward developing more active HOR catalysts and elucidating the reaction

mechanism. With the advent of highly active catalysts, however, the intrinsically slow HOR kinetics no longer appeared to be the dominant performance-limiting factor. Improved water management within the cell was proposed as a key contributor to the enhanced AEMFC performance. Yet, this explanation alone seemed insufficient, as high peak power densities have been achieved even in cells with suboptimal water management. In this context, two specific adsorptions on the Pt group metal catalyst were identified as performance-limiting factors for AAEMFCs anodes, namely: i) cation-hydroxide-water co-adsorption and ii) phenyl group adsorption.

2.2.4. Cation-hydroxide-water co-adsorption

The cationic functional groups of the ionomer can strongly interact with catalyst surfaces. Such interactions may lead to partial coverage of active sites, thereby reducing the electrochemically accessible surface area and hindering hydrogen adsorption and oxidation. Moreover, the presence of adsorbed ionomer species can alter the local distribution of hydroxide ions and reaction intermediates, further impacting HOR kinetics. Given that the HOR in alkaline media is intrinsically more sensitive to surface chemistry and interfacial structure than in acidic systems, even subtle ionomer–catalyst interactions can translate into significant performance losses[111].

2.2.5. Phenyl group adsorption

Phenyl groups in some binders may adsorb onto catalysts, altering the electrochemical interface. Controlling this adsorption is critical to optimizing catalytic efficiency. Matanovic *et al.* tested how the performance of AAEMFCs significantly changes depending on the backbone structure of polyaromatic ionomer or the type of the catalyst used at the anode. For the same anode catalyst, the performance decreases in the order poly(fluorene) > poly(p-biphenyl alkylene) > poly(terphenyl alkylene)s, which is in agreement with the decrease in the DFT-calculated interaction energies between the catalyst surface and the corresponding ionomer fragment a shown in Fig. 6.

The trend in the adsorption energies is explained on the basis of the structural and conformational features of the ionomer fragments: strong adsorption of the polyaromatic ionomer fragments correlates with the number of benzene rings with a low rotational barrier that can bind parallel to the metal surfaces, leading to strong interaction and hybridization of the aromatic π-orbitals with metal electronic states. It emerges that the interaction between the ionomer and electrocatalyst should also receive pivotal attention when designing high-performing ionomers[112].

Therefore, beyond catalyst activity and membrane properties, the physicochemical nature of the ionomer and its interfacial behavior with HOR catalysts must be carefully considered to fully understand and optimize AEMFC performance.

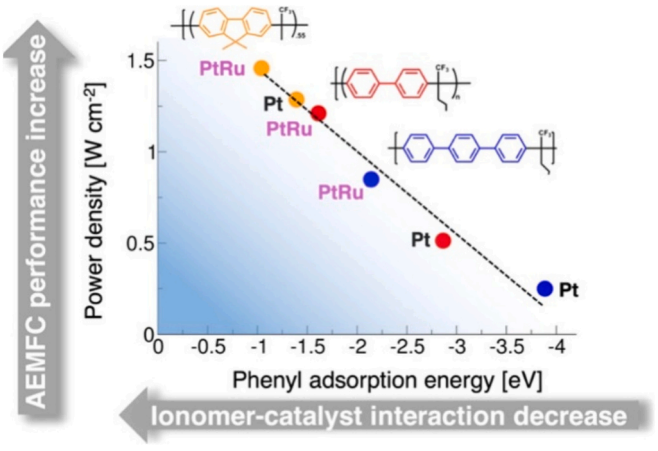


Fig. 6. Correlation between the phenyl adsorption energy and the performance of AAEMFCs. Reproduced from Matanovic et al.[112] with all permissions.

2.3. Electrochemical Oxidation of Phenyl in an AEMFC Cathode and AEMWE Anode

Another key aspect in the design of ionomeric binders for AAEMWEs is their resistance to electrochemical oxidation[113]. Li et al. demonstrated that electrochemical oxidation of phenyl groups adsorbed on OER catalysts leads to the formation of phenol, which can contribute to performance losses in AEM electrolyzers. This degradation is attributed to the acidic nature of phenol (pKa = 9.6), which lowers the local pH by neutralizing the quaternary ammonium hydroxide groups of the ionomer. Such acid–base interactions are particularly detrimental in alkaline systems. The formation of phenol can be mitigated by employing ionomeric binders containing highly substituted phenyl groups, which exhibit lower adsorption energies on the catalyst surface and are therefore less prone to oxidative degradation[114].

3. PIMs as alternative binders: a general overview

PIMs are a relatively recent class of macromolecules. They were first disclosed in a patent application in 2003 and subsequently reported in scientific literature in 2004[115] and they have been used for plenty of applications[116–118]. According to the IUPAC classification, micropores are defined as pores with diameters smaller than 2 nm. Intrinsic microporosity in polymers refers to a continuous network of interconnected intermolecular voids that arises directly from the shape and rigidity of the constituent macromolecules[119].

The formation of stable micropores within a polymeric structure requires overcoming the cohesive attractive forces between adjacent chains or neighboring segments of the same chain, which would otherwise promote dense packing and pore collapse. Conventional polymers generally possess sufficient conformational flexibility to rearrange and maximize intermolecular interactions, resulting in efficient packing and limited free volume. In contrast, PIMs are specifically designed with highly rigid and contorted molecular architectures that hinder efficient packing and generate significant intrinsic free volume[120]. PIMs are typically synthesized via step-growth polymerization of aromatic monomers, in which each monomer forms multiple covalent bonds within the polymer backbone. The chains are constructed from aromatic rings connected by spirocyclic, bridged bicyclic, or other fused-ring units that impose rigid two- or three-dimensional random-coil conformations. When single bonds are present (e.g., imide C–N bonds), steric hindrance restricts rotational freedom between adjacent aromatic units, preserving the contorted structure and maintaining the intrinsic microporosity as summarized in Fig. 7

PIMs have attracted increasing attention as ionomer binders due to unique structural features: the intrinsic microporosity can facilitate mass transport within the CL by providing permeable pathways for reactant gases and by reducing diffusion limitations that often arise when conventional polymeric binders partially block access to catalytic sites. In addition, the rigid backbone plays a crucial role in preserving the microporous structure and promoting size selectivity for gases and ions. An additional advantage lies in their chemical versatility, as their structure can be modified through the introduction of ionic functionalities such as sulfonic acid or quaternary ammonium groups, allowing the development of ionomers capable of conducting protons or anions. Lastly, PIMs are readily processable from solution into practical forms, including membranes that function as efficient molecular sieves.

Contrary to conventional porous materials, the microporosity of PIMs does not arise from permanent inorganic pores or from a template but from the rigid polymer chains unable to efficiently packing at the molecular level. Accordingly, the excess free volume provides interconnected pathways for molecular transport and represents the defining structural feature of this class of materials[121].

As shown in Fig. 8, the most representative architectures are

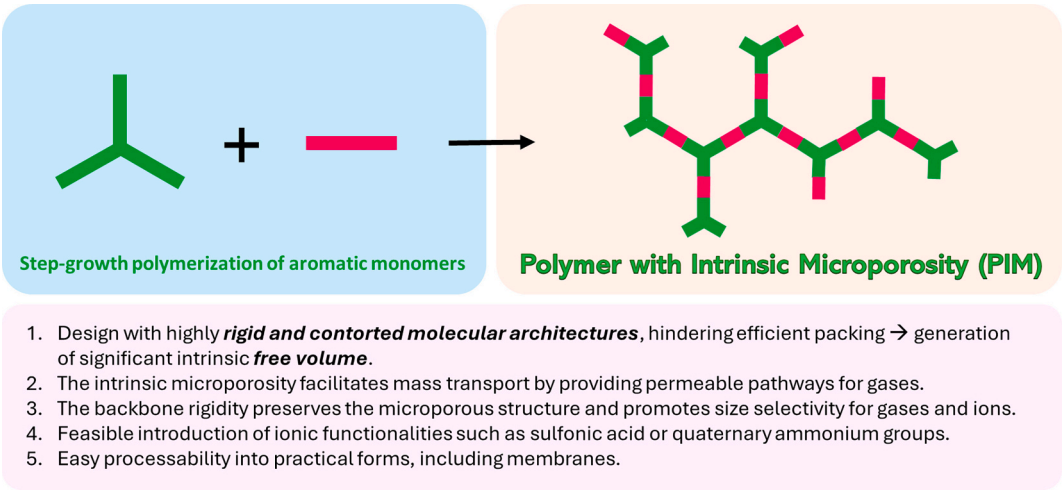


Fig. 7. Scheme of PIMs production and chemical features.

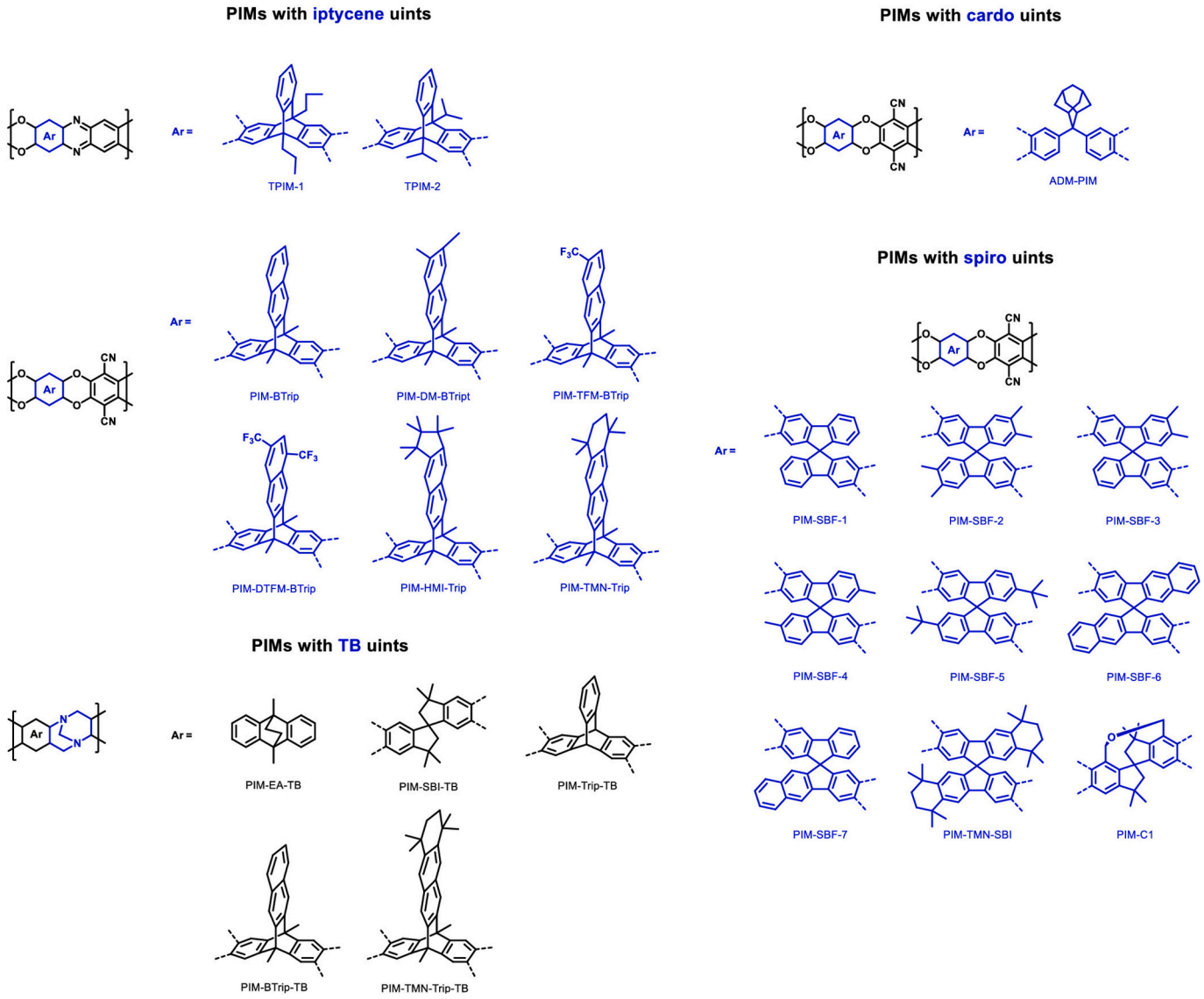


Fig. 8. Scaffolds of PIMs with different molecualr achitectures based on iptcene, cardo and spiro units. Reprinted with permission from [122]. Copyright © 2020 Wiley Periodicals, Inc.

iptycene, cardo and spiro-centered structures. The free volume generated by these rigid molecular architectures is a non-equilibrium structural state and can be influenced by polymer processing, solvent history, temperature, functionalization and long-term physical aging. The relevance of molecular-design is allow to maximize the fractional free volume generating accessible, interconnected and sufficiently stable free-volume elements that can provide the desired transport properties and this is of particular relevance for binding applications.

The principal limitation associated with intrinsic microporosity represented by the thermodynamically metastable glassy state rather than a permanently rigid pore network[123]. Accordingly, polymer chains progressively relax toward denser configurations, reducing the accessible free volume and consequently decreasing gas permeability. This physical-aging process is particularly relevant to PIM binders because catalyst layers are expected to operate for thousands of hours. A mechanistic understanding of aging requires coupling macroscopic transport measurements with probes of polymer dynamics as nuclear magnetic resonance (NMR) techniques. Solid-state ^{13}C NMR spin–lattice relaxation times provide information on local molecular mobility and can be used to distinguish changes in segmental dynamics from purely morphological effects and it was used for studing hyper-crosslinked polymers mixed with PIM-1as reported by Begni et al.[124]. Authors reported that PIM-1/hyper-crosslinked polymer blends reduce long-term permeability decay relative to pristine PIM-1 reducing at the same time the system permeability.

Physical aging should be treated as a kinetic design parameters to be considered during the binder design rather than an unavoidable post-processing defect, and future PIM binders should be evaluated using time-dependent transport measurements, relaxation spectroscopy, and catalyst-layer testing after controlled thermal, solvent, and electrochemical conditioning.

Furthermore, the very same rigid molecular architecture accountable for the intrinsic microporosity can result in limited solubility, slow dissolution, and strong sensitivity to solvent history. These effects are particularly relevant for the ink preparation that ruled the polymer aggregation, catalyst dispersion, drying kinetics, ionomer redistribution, and the mesoscale pore architecture[125]. Recent efforts toward greener PIM synthesis and processing demonstrate that solvent selection can be incorporated into molecular design rather than treated as a downstream manufacturing problem. Water/isopropanol processing of pPIM is particularly relevant because it demonstrates that an ionomer can be engineered simultaneously for ionic functionality, intrinsic microporosity and compatibility with lower-hazard solvent systems [126]. This was in accordance with the 12 principles of green chemistry and can provide a useful framework for the evaluation of sustainability of PIM binders that involved the use of benign solvents, wastewater minimization, reproducibility, process monitoring, resource efficiency and end-of-life considerations[127].

4. PIMs as binder: applications

The role of PIM in electrocatalysis extends beyond conventional descriptions based solely on Fick diffusion laws as recent electrochemical measurements have demonstrated for PIM-1-based Pt systems [128]. Authors reported that deposited Pt can act synergically with PIM-1 as reservoir for gaseous O_2 modifying both the concentration and transport of O_2 at the cathode/electrolyte interface. Nevertheless, authors also reported that, under ambient oxygen conditions, the apparent oxygen concentration associated with the PIM-1 nanoparticle film increased from approximately 0.3 mM in the aqueous electrolyte to 50 ± 5 mM together with a decrement of the apparent oxygen from 2.8×10^{-9} down to 1.6×10^{-12} m^2 s^{-1}. The simultaneous local concentration increment and reduced diffusivity of O_2 highlighted an important distinction between molecular storage, partitioning, and transport in microporous polymers. The PIM-1 layer did not simply provide a high-diffusivity pathway for oxygen but promoted a local partitioning and storage of O_2 at the electrode surface. The resulting modification of the local concentration field can enhance the availability of oxygen to the Pt surface and consequently alter the electrochemical response. The relevant transport problem involved at least three coupled processes: partitioning of the reactant between the aqueous and polymer phases, storage within the microporous polymer and release and diffusion toward the catalytic surface expanding the PIMs role from passive gas-permeable binders to active molecular reservoirs that modify the local reaction environment.

4.1. Fuel cells

The utilization of PIMs for fuel cell applications has been reported by Choi et al.[129] using poly(arylene ether sulfone) with spirobisindane modification (SBI-PES), alongside a series of PESs (QOH-SBIs) featuring pendant moieties of spirobisindane and tetra(quaternary ammonium) hydroxide to serve as electrode binders for solid alkaline exchange membrane fuel cells (SAEMFC). To understand the influence of spirobiindane units, gas permeability of SBI-PES in comparison to the pristine polymer was studied and most importantly they investigate the structural role played by the spirobiindane group within the binder framework. As previously demonstrated, the polymer electrolyte binder featuring the spirobisindane moiety, with exceptional gas permeability, exhibited superior cell performance when compared to counterparts lacking this distinctive moiety [130]. Overall, the fuel cell performance was directly affected by the binder gas permeability. The results of this study confirm that the presence of spirobiindane moieties in polymer backbone helps increase gas permeability and overall the SAEMFC performance.

Mass transport in electrode is one of the main factors limiting the use of low Pt loading. The creation of binder with improved gas permeability can be key in developing FCs with little loading of Pt. To this extend, Sun et al. [126] developed a phosphonated ionomers of intrinsic microporosity (pPIM) for High-Temperature Proton Exchange Membrane Fuel Cells (HTPEMFCs) to overcome the high mass transport resistance within the catalyst layer which is one of the major factor limiting the use of a low Pt loadings in PEMFCs.

pPIM represented an important conceptual evolution beyond the traditional view of PIMs as amorphous polymers containing randomly distributed free volume. The pPIM partially ordered architecture was due to the organization of functional groups along the rigid polymer backbone abled to creating a more defined molecular environment[47].

To be noted, the operation temperature of HTPEMFCs is 120−250 °C, providing particular advantages as faster reaction kinetics at the electrodes, higher tolerance to CO, and better water and heat management[131].

Sun et al.[126] synthetized a partially ordered pPIM, having both proton-conductive functionality and intrinsic microporosity creating gas transmission channel, to be used as the catalyst binder to improve the mass transport of electrodes. On the other hand, the phosphonated groups provide proton conduction. Under H_2/O_2 conditions at 160°C, the membrane electrode assembly featuring the pPIM ionomer exhibits a peak peak power density reaching 506.6 mW cm^{-2}, which is 18% to 379% greater than commercial or other porous catalyst binders. The partially ordered structure of pPIM, which is due to the assembly of the -PO_3H_2 groups, facilitate the stable conduction of gases and protons providing an ideal mass transport pathways. Consequently, this accelerates redox reactions, particularly the oxygen reduction reaction (ORR) within the cathode. pPIM has intrinsic micropores to provide a robust gas transmission channels, while the -PO_3H_2 groups allow proton conduction sites. The SBI (spirobisindane) units decrease the phenyl contents of the Polyaromatic Backbone present in other commercially available ionomers, which decrease the negative phenyl group adsorption [112,132]. Hence the gas permeability, proton conductivity, and interfacial compatibility of the ionomer with the catalyst to obtain good dispersibility in catalyst inks, is crucial to improve the performance of

ionomers. Another important intermediate strategy is represented by fluorine-lean pPIM[47] for PEMFC. Authors reported that an ionomer loading up to 0.2 wt.% improved O_2 diffusion over the Nafion-based CL while excessive ionomer content increased water uptake and blocked transport pathways. This study suggested that the optimum binder composition was ruled by a balance between diffusion, coverage, and mass transport.

Li et al.[133] research group also focused on developing a tetrazole functionalized PIM binder which allow the loading reduction of noble-metal catalysts such as Pt Loading, which it is a challenge when using commercially available binder or other types of polymers such as phosphoric acid doped polybenzimidazole.

When phosphoric acid is used as electrolyte in HTPEMFCs, at a temperature of 160°C, the platinum surface exhibits robust bonding with acid molecules (H_3PO_4) at lower potentials (300–400 mV), as well as with acid anions ($H_2PO_4^-$) at intermediate potentials (700–800 mV) throughout the cell operation of the cell [134–137], forcing the use of a high Pt loading for the electrode preparation in the range 0.5–1.0 mg_{Pt} cm^{-2}, usually around 0.7 mg_{Pt} cm^{-2} [138]. The reason to use a high Pt loading is the low electrode performance and poor mass transport and Pt poisoning due to the acid absorption on the metal surface. The H-bonding functionalities of the reported PIMs, improve the binding energy of Phosphoric acid mitigating the adsorption of phosphoric acid on the Pt surface.

The use of a tetrazole functionalized PIM binder allow an H_2-O_2 cell to reach a high Pt-mass specific peak power density of 3.8W mgPt−1 at 160 °C with a little Pt loading of 0.15 mgPt cm^{-2}. Instead the Pt loading in the low temperature PEMFC is lower being about 0.3 mgPt cm^{-2} and aiming at 0.15mgPt cm^{-2}, with an estimated Pt consumption as high as 70–85% [38,139].

Tetrazole-functionalized PIM binders provided an example in which molecular functionality modifies catalyst utilization through competitive interfacial interactions. In phosphoric acid-doped based HTPEMFCs, phosphate-containing species can interact strongly with Pt occupying catalytically relevant surface sites, while the introduction of tetrazole groups provided multiple nitrogen sites able to strongly interact with phosphoric-acid species. Accordingly, the incorporation into a rigid microporous backbone promoted the localization of acidic sites retaining the gas-transport pathways[140].

In HTPEMFCs, the commonly used binder materials are PBI, polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF), that play a pivotal role in facilitating the formation of triple phase boundaries by promoting the diffusion of acid from the membrane. Nonetheless, the utilization of these binders introduces several challenges. Firstly, they cause partial obstruction of catalyst sites, thereby decreasing the Pt performance. Secondly, all these binder materials typically exhibit dense characteristics, thereby limiting the efficient dissolution and diffusion of reactant gases. Consequently, their effective transport to the catalytic sites becomes difficult [141,142]. Burba et al. [143] proved the feasibility of PIM-1 use ad binder for fuel celling slightly acidic environment using a low loading of binder.

Interestingly, the original PIM-1 can be used as platform for the preparation of improved binders through simple post-synthesis modifications. Kim et al.[144] produced a sulphonated PIM-1 that was to brittle for the production of membranes but can be used by mixing with neat PIM-1 as high oxygen permeable binder for fuel cell.

A particularly important development is represented by sulfonated polyxanthene (SPX) which proved how microporosity can be used to regulate the distribution of the ionic phase rather than simply enhancing gas permeability[145]. The rigid and contorted SPX architecture promoted the formation of sub-nanometric transport domains in which sulfonic-acid functionalities can interact with phosphoric acid. This confinement induced the retention of the acid within the CL and reduced uncontrolled redistribution or acid loss during high-temperature operation. The resulting electrode architecture achieved a power density of up to 805 mW cm^{-2} at 180 °C.

4.2. Electrolyzer

The use of PIMs has spread around for fuel cell applications while the their utilization as binders for electrolyzers is still limited with few examples in literature.

The deployment of PIMs as binders in both water and CO_2 electrolyzers can be a significant step forward in the design of high-performance electrochemical systems due to the mass transport efficiency due to the extended porous network.

Khalid et al.[146] developed a PIM-1 based AEM water electrolyzers, abled to efficiently transport hydroxide ions. Authors reported an increased ion conductive of a commercial blended with PIM-1 and increment of water permeability with the increment of PIM-1 amount with a maximum at 50 wt.% loading. Wang et al.[147] developed two functionalized PIMs tailored with pyrrolidinium (QPPIMy) and piperidinium (QPPIMi) cations for AEM water electrolyzers. The hydrogen permeabilities of QPPIMy and QPPIMi membranes were up to 61 and 32 barrer, which were significantly higher than control binder selected. Authors also reported a that a loading of QPPIMy up to 10 wt.% reached a current density of up to 2000 mA/cm^2 at a voltage of 2.04 V.

Nonetheless, alkaline stability represents a critical unresolved issue for PIM-based anion-conducting architectures. Short-term retention of conductivity or cell voltage demonstrates operational stability but did not establish preservation of the molecular structure. Microporosity itself plays an ambiguous effect on durability with the increment of internal surface area that could provide greater access of hydroxide, water, and reactive intermediates to chemically active sites, potentially accelerating degradation. Conversely, rigid backbones may suppress swelling and limit the conformational rearrangements associated with degradation. Whether intrinsic microporosity accelerates or suppresses degradation is therefore an empirical question, not a universal consequence of the PIM architecture. The field currently lacks sufficiently standardized extended durability datasets under realistic alkaline operating conditions. This is arguably one of the most important barriers preventing PIMs from progressing from promising electrode materials to robust industrial ionomers.

Recently, Perry et al.[148] reported that the use of 0.01 mg cm^{-2} loading of PIMs increased the activity, selectivity and stability of a copper towards ethylene production during CO_2 reduction. Authors suggested that the mechanism laying behind was analogous to the one reported by Madrid et al.[149] for ORR with the PIM layer that stored the dissolved CO_2 in a triphasic environment for facile reduction. Nevertheless, a high loading of PIMs reduced the hydrophobicity by increasing the water reduction competing with CO_2 reduction, finally reducing the ethylene yield.

In table 3, a comparative analysis of main PIM-based binders for different electrocatalytic applications is reported.

The quantitative comparison shows why a single permeability or conductivity value is insufficient to rank PIM binders. Reported data are obtained under different temperatures, relative humidities, electrolytes, catalyst loadings and binder-to-catalyst ratios; therefore, values should not be interpreted as a universal ranking. In particular, membrane permeability values are useful descriptors of molecular transport potential but cannot be directly substituted for CL oxygen transport resistance.

5. Conclusions: limitations and future perspectives of PIMs utilization

PIMs represent a prosing platform as binders in electrocatalytic systems due to a combination of physicochemical, electrochemical, and structural properties. Furthermore, key limitations are their relatively poor chemical and electrochemical stability in harsh environments, particularly under strong oxidative or reductive potentials typical of oxygen evolution or hydrogen evolution reactions where several degradative mechanism are active including backbone degradation and

Table 3
Quantitative benchmarking of representative PIM and PIM-derived binder systems reported in the literature.

Binder name	Application	Functionalities	Properties	Key limitation	Reference
PIM-1	ORR binder; acidic/ alkaline RDE	▪ Cyanide ▪ Non ionic	▪ O_2 permeability of up to 1300 Barrer at 25 °C f ▪ Alkaline ORR mass activity up to 22 mA $mgPt^{-1}$ with binder a loading of 0.1 wt.%	▪ Performance depends strongly on binder loading ▪ Excessive loading decreases kinetic/ transport phenomena	[143]
pPIM	HT-PEMFC binder	▪ Phosphonic acid	▪ 74 mS cm−1 at 160 °C, humidified ▪ 507 mW cm^{-2} at 180 °C	▪ High rigidity can limit ion mobility ▪ Limited durability	[126]
Tetrazole-PIM	HT-PEMFC binder	▪ Tetrazole ▪ H-bonding groups	▪ 3.8 W $mgPt^{-1}$ at 160 °C ▪ Proton conduction in phosphoric acid environment	▪ Pt utilization around 25% ▪ Leaching in acidic environment	[133]
SPX	HT-PEMFC binder	▪ Sulfonic residues	▪ 83.6–180 mS cm^{-1} at 80 °C ▪ 805 mW cm^{-2} at 180 °C; Pt utilization 42.51%	▪ Performance decreases above 180 °C	[145]
Fluorine-lean pPIM	PEMFC CL ionomer	▪ Phosphonic acid ▪ Fluorine-lean backbone	▪ Higher O_2 diffusion coefficient than Nafion ▪ L at I:C = 0.2 ▪ Proton-conducting	▪ Higher water uptake ▪ Brittleness	[47]
PIM-1/SEBS-DABCO	AEMWE binder blend	▪ Quaternary ammonium ▪ Cynide	▪ Water permeability increases with PIM-1 fraction ▪ Over 270 h stability	▪ Onset of degradation in 1 M KOH at 60 °C	[146]
QPPIMy / QPPIMi	AEMWE ionomer	▪ Pyrrolidinium ▪ Piperidinium	▪ H_2 permeability of up to 61 Barrer ▪ OH^- conducting ▪ 2000 mA cm^{-2} at 2.04 V	▪ Limited conductivity	[147]

oxidation of side chains. Nevertheless, PIMs show promising filming properties preserving at the same time a great electrochemical surface area. Furthermore, the tunability of PIMs backbone design and functional group represents an astonishing tool to produce fluorine free next generation of binder platform compatible with complex electrode architectures.

PIMs binders will represent a powerful tool for the design of high-performance, durable, and efficient electrochemical systems, supporting the broader transition toward sustainable energy technologies.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be available upon request to the authors.

References

[1] M.B. Hossain, M.R. Islam, K.M. Muttaqi, D. Sutanto, A.P. Agalgaonkar, Advancement of fuel cells and electrolyzers technologies and their applications to renewable-rich power grids, J. Energy Storage 62 (2023) 106842.
[2] N. Sazali, W.N. Wan Salleh, A.S. Jamaludin, M.N. Mhd Razali, New perspectives on fuel cell technology: A brief review, Membranes 10 (2020) 99.
[3] V.M. Lopez, H. Ziar, J. Haverkort, M. Zeman, O. Isabella, Dynamic operation of water electrolyzers: A review for applications in photovoltaic systems integration, Renew. Sust. Energ. Rev. 182 (2023) 113407.
[4] A.L. Santos, M.-J. Cebola, D.M. Santos, Towards the hydrogen economy—A review of the parameters that influence the efficiency of alkaline water electrolyzers, Energies 14 (2021) 3193.
[5] C.P. O’Brien, R.K. Miao, A. Shayesteh Zeraati, G. Lee, E.H. Sargent, D. Sinton, CO2 electrolyzers, Chem. Rev. 124 (2024) 3648–3693.
[6] T.A. Suter, K. Smith, J. Hack, L. Rasha, Z. Rana, G.M.A. Angel, et al., Engineering catalyst layers for next-generation polymer electrolyte fuel cells: A review of design, materials, and methods, Adv. Energy Mater. 11 (2021) 2101025.
[7] W. Yu, F. Luo, X. Liang, C. Jiang, Y. Xu, Z. Liu, et al., Ionomeric binders in polymer electrolyte fuel cells: roles, challenges, and advances, Chem. Soc. Rev. 54 (2025) 9407–9456.
[8] H. Chen, M. Ling, L. Hencz, H.Y. Ling, G. Li, Z. Lin, et al., Exploring chemical, mechanical, and electrical functionalities of binders for advanced energy-storage devices, Chem. Rev. 118 (2018) 8936–8982.
[9] F. Habibzadeh, P. Mardle, N. Zhao, H.D. Riley, D.A. Salvatore, C.P. Berlinguette, et al., Ion exchange membranes in electrochemical CO2 reduction processes, Electrochem. Energy Rev. 6 (2023) 26.
[10] P. Zuo, Z. Xu, Q. Zhu, J. Ran, L. Ge, X. Ge, et al., Ion exchange membranes: constructing and tuning ion transport channels, Adv. Funct. Mater. 32 (2022) 2207366.
[11] K. Zhang, X. Liang, L. Wang, K. Sun, Y. Wang, Z. Xie, et al., Status and perspectives of key materials for PEM electrolyzer, Nano res energy. 1 (2022) e9120032.
[12] Y. Wang, Y. Pang, H. Xu, A. Martinez, K.S. Chen, PEM Fuel cell and electrolysis cell technologies and hydrogen infrastructure development–a review, Energy Environ. Sci. 15 (2022) 2288–2328.
[13] S. Mo, L. Du, Z. Huang, J. Chen, Y. Zhou, P. Wu, et al., Recent advances on PEM fuel cells: from key materials to membrane electrode assembly, Electrochem. Energy Rev. 6 (2023) 28.
[14] A. Sahul Hameed, S. Munusamy, R. Gokulapriyan, D.J. Yoo, Comprehensive review of anion exchange membrane with ether and ether-free backbone, ACS Appl. Polym. Mater. 6 (2024) 12341–12361.
[15] G. Sriram, K. Dhanabalan, K.V. Ajeya, K. Aruchamy, Y.C. Ching, T.H. Oh, et al., Recent progress in anion exchange membranes (AEMs) in water electrolysis:

synthesis, physio-chemical analysis, properties, and applications, J. Mater. Chem. A 11 (2023) 20886–21008.
[16] G. Das, J.-H. Choi, P.K.T. Nguyen, D.-J. Kim, Y.S. Yoon, Anion exchange membranes for fuel cell application: a review, Polymers 14 (2022) 1197.
[17] J. Zhao, H. Liu, X. Li, Structure, property, and performance of catalyst layers in proton exchange membrane fuel cells, Electrochem. Energy Rev. 6 (2023) 13.
[18] E.K. Volk, M.E. Kreider, S. Kwon, S.M. Alia, Recent progress in understanding the catalyst layer in anion exchange membrane electrolyzers–durability, utilization, and integration, EES Catal. 2 (2024) 109–137.
[19] M. Gutiérrez-Roa, D. Sebastián, H. Guzmán, F. Zammillo, M. Gallone, S. Hernández, et al., Tuning the activity and selectivity of CuPt/C catalysts for the electrochemical CO2 reduction, J. CO_2 Util. 95 (2025) 103084.
[20] G. Cuatto, M. Zoli, M. Gallone, H. Guzmán, M. Castellino, S. Hernández, Standardization of Cu2O nanocubes synthesis: Role of precipitation process parameters on physico-chemical and photo-electrocatalytic properties, Chem. Eng. Res. Des. 199 (2023) 384–398.
[21] M. Etzi, A. Mezza, V. Bugliarelli, J. Dangbegnon, D. Sassone, M. Bartoli, et al., Size-Dependent Selectivity of Cu2O Nanocube Catalysts for CO2 Reduction at Industrial Current Densities, Electrochim. Acta 148114 (2026).
[22] T. Zhang, L. Meng, C. Chen, L. Du, N. Wang, L. Xing, et al., Similarities and differences between gas diffusion layers used in proton exchange membrane fuel cell and water electrolysis for material and mass transport, Adv. Sci. 11 (2024) 2309440.
[23] D. Chen, P. Pei, Y. Li, P. Ren, Y. Meng, X. Song, et al., Proton exchange membrane fuel cell stack consistency: Evaluation methods, influencing factors, membrane electrode assembly parameters and improvement measures, Energy Convers. Manag. 261 (2022) 115651.
[24] L. Shi, D. Liu, X. Lin, R. Cheng, F. Liu, C. Kim, et al., Stable and High-performance Flow H2-O2 Fuel Cells With Coupled Acidic Oxygen Reduction and Alkaline Hydrogen Oxidation Reactions, Adv. Mater. 36 (2024) 2314077.
[25] E. Fabbri, T.J. Schmidt, Oxygen evolution reaction—the enigma in water electrolysis, ACS Publications, 2018, pp. 9765–9774.
[26] J.P. Hughes, J. Clipsham, H. Chavushoglu, S.J. Rowley-Neale, C.E. Banks, Polymer electrolyte electrolysis: A review of the activity and stability of non-precious metal hydrogen evolution reaction and oxygen evolution reaction catalysts, Renew. Sust. Energ. Rev. 139 (2021) 110709.
[27] M. Huang, A. Ozden, Oxygen Evolution Reaction Catalysts for Acidic-Media CO2 Electrolyzers. Advanced Materials.n/a:e72644, 2026.
[28] M. Gallone, A. Fortunati, S. Hernández, Assessing the CO2 Capture and Electro-Reduction in Imidazolium-Based Ionic Liquids: Role of the Ion Exchange Membrane, Catalysts 15 (2025) 318.
[29] R. O'Hayre, D.M. Barnett, F.B. Prinz, The Triple Phase Boundary: A Mathematical Model and Experimental Investigations for Fuel Cells, J. Electrochem. Soc. 152 (2005) A439.
[30] Y. Xu, T. Yan, X. Zhang, W. Liu, Y. Meng, J. Lin, et al., Triple-phase interfaces for electrochemical reduction of carbon dioxide, Chem. Soc. Rev. 55 (2026) 2366–2395.
[31] D. Chen, L. Lu, J. Li, Z. Yu, W. Kong, H. Zhu, Percolation micro-model to predict the effective properties of the composite electrode with poly-dispersed particle sizes, J. Power Sources 196 (2011) 3178–3185.
[32] X. Lu, T.M. Heenan, J.J. Bailey, T. Li, K. Li, D.J. Brett, et al., Correlation between triple phase boundary and the microstructure of solid oxide fuel cell anodes: the role of composition, porosity and Ni densification, J. Power Sources 365 (2017) 210–219.
[33] B. Zhang, H. Gao, C. Xiao, X. Tong, Y. Chen, The trade-off between membrane permselectivity and conductivity: A percolation simulation of mass transport, J. Membr. Sci. 597 (2020) 117751.
[34] Y.S. Kim, Hydrocarbon ionomeric binders for fuel cells and electrolyzers, Adv. Sci. 10 (2023) 2303914.
[35] C. Zhou, M.A. Guerra, Z.-M. Qiu, T.A. Zawodzinski, D.A. Schiraldi, Chemical durability studies of perfluorinated sulfonic acid polymers and model compounds under mimic fuel cell conditions, Macromolecules 40 (2007) 8695–8707.
[36] E.O. Balogun, N. Hussain, J. Chamier, P. Barendse, Performance and durability studies of perfluorosulfonic acid ionomers as binders in PEMFC catalyst layers using Electrochemical Impedance Spectroscopy, Int. J. Hydrog. Energy 44 (2019) 32219–32230.
[37] C. Bas, L. Flandin, A.-S. Danerol, E. Claude, E. Rossinot, N.D. Alberola, Changes in the chemical structure and properties of a perfluorosulfonated acid membrane induced by fuel-cell operation, J. Appl. Polym. Sci. 117 (2010) 2121–2132.
[38] A. Kusoglu, A.Z. Weber, New Insights into Perfluorinated Sulfonic-Acid Ionomers, Chem. Rev. 117 (2017) 987–1104.
[39] R. Lohmann, R.J. Letcher, The universe of fluorinated polymers and polymeric substances and potential environmental impacts and concerns, Curr. Opin. Green Sustainable Chem. 41 (2023) 100795.
[40] T. Li, J. Shen, G. Chen, S. Guo, G. Xie, Performance comparison of proton exchange membrane fuel cells with nafion and aquivion perfluorosulfonic acids with different equivalent weights as the electrode binders, ACS Omega 5 (2020) 17628–17636.
[41] S. Banerjee, D.E. Curtin, Nafion® perfluorinated membranes in fuel cells, J. Fluor. Chem. 125 (2004) 1211–1216.
[42] W.G. Grot, Nafion® membrane and its applications. Electrochemistry in Industry, Springer, New Directions, 1982, pp. 73–87.
[43] E. Balogun, M. Adamski, S. Holdcroft, Communication—non-fluorous, hydrocarbon PEMFCs, generating> 1 W cm− 2 power, J. Electrochem. Soc. 167 (2020) 084502.
[44] M. Adamski, T.J. Skalski, B. Britton, T.J. Peckham, L. Metzler, S. Holdcroft, Highly stable, low gas crossover, proton-conducting phenylated polyphenylenes, Angew. Chem. 129 (2017) 9186–9189.
[45] N.B. McKeown, Polymers of Intrinsic Microporosity, Int. Sch. Res. Not. 2012 (2012) 513986.
[46] L. Xian, L. Wu, T. Xu, Role of ionomer in membrane electrode assembly for proton exchange membrane fuel cells, Sci. Sin. Chim. 48 (2018) 1040–1057.
[47] T. Stigler, T. Nemeth, P. Fortin, S. Thiele, J. Kerres, Fluorine-Lean Phosphonated Polymers of Intrinsic Microporosity with High Oxygen Permeability as a PEMFC Catalyst Layer Ionomer, ACS Appl. Energy Mater. 8 (2025) 4629–4639.
[48] B.-S. Kim, J.-H. Park, J.-S. Park, Effect of blended perfluorinated sulfonic acid ionomer binder on the performance of catalyst layers in polymer electrolyte membrane fuel cells, Membranes 13 (2023) 794.
[49] C. Zhao, S. Yuan, X. Cheng, L. An, J. Li, S. Shen, et al., Effect of perfluorosulfonic acid ionomer in anode catalyst layer on proton exchange membrane water electrolyzer performance, J. Power Sources 580 (2023) 233413.
[50] J. Peron, Z. Shi, S. Holdcroft, Hydrocarbon proton conducting polymers for fuel cell catalyst layers, Energy Environ. Sci. 4 (2011) 1575–1591.
[51] A. Sarapuu, E. Kibena-Põldsepp, M. Borghei, K. Tammeveski, Electrocatalysis of oxygen reduction on heteroatom-doped nanocarbons and transition metal–nitrogen–carbon catalysts for alkaline membrane fuel cells, J. Mater. Chem. A 6 (2018) 776–804.
[52] L. Cui, L. Cui, Z. Li, J. Zhang, H. Wang, S. Lu, et al., A copper single-atom catalyst towards efficient and durable oxygen reduction for fuel cells, J. Mater. Chem. A 7 (2019) 16690–16695.
[53] E. Cossar, A.O. Barnett, F. Seland, R. Safari, G.A. Botton, E.A. Baranova, Ionomer content optimization in nickel-iron-based anodes with and without ceria for anion exchange membrane water electrolysis, J. Power Sources 514 (2021) 230563.
[54] L. Liu, Y. Lu, C. Ning, N. Li, S. Chen, Z. Hu, Comb-shaped sulfonated poly (aryl ether sulfone) proton exchange membrane for fuel cell applications, Int. J. Hydrog. Energy 47 (2022) 16249–16261.
[55] A. Raut, H. Fang, Y.-C. Lin, D. Sprouster, Y. Yin, Y. Fang, et al., Effect of membrane mechanics on AEM fuel cell performance, Energy Advances 2 (2023) 113–122.
[56] S. Gottesfeld, D.R. Dekel, M. Page, C. Bae, Y. Yan, P. Zelenay, et al., Anion exchange membrane fuel cells: Current status and remaining challenges, J. Power Sources 375 (2018) 170–184.
[57] D. Henkensmeier, M. Najibah, C. Harms, J. Žitka, J. Hnát, K. Bouzek, Overview: state-of-the art commercial membranes for anion exchange membrane water electrolysis, J. Electrochem. Energy Convers. Storage 18 (2021) 024001.
[58] C. Hu, J.H. Park, N.Y. Kang, X. Zhang, Y.J. Lee, S.W. Jeong, et al., Effects of hydrophobic side chains in poly(fluorenyl-co-aryl piperidinium) ionomers for durable anion exchange membrane fuel cells, J. Mater. Chem. A 11 (2023) 2031–2041.
[59] H. Altinisik, C. Celebi, A. Ozden, Y. Devrim, C.O. Colpan, A review on membranes for anion exchange membrane water electrolyzers, Renew. Sust. Energ. Rev. 226 (2026) 116277.
[60] S. Hong, P.J. Kenis, Ultrathin Microporous Interlayer in a Membrane Electrode Assembly Cell for Efficient and Scalable Electroreduction of CO2 to Formate, ACS Energy Letters 11 (5) (2026) 3897–3906.
[61] L. Gatti, S. Verhovez, A. Mezza, M. Etzi, S. Stassi, C.F. Pirri, et al., Role of the Binder in Mitigating Salt Deposition in 100 cm2 Membrane Electrode Assembly CO2 Electrolyzers, Adv. Energy Sustainability Res. 6 (2025) e202500312.
[62] X. Yan, Z. Xu, S. Yuan, A. Han, Y. Shen, X. Cheng, et al., Structural and transport properties of ultrathin perfluorosulfonic acid ionomer film in proton exchange membrane fuel cell catalyst layer: A review, J. Power Sources 536 (2022) 231523.
[63] M. Eikerling, Water management in cathode catalyst layers of PEM fuel cells: a structure-based model, J. Electrochem. Soc. 153 (2006) E58–E70.
[64] K. Jiao, X. Li, Water transport in polymer electrolyte membrane fuel cells, Prog. Energy Combust. Sci. 37 (2011) 221–291.
[65] W. Dai, H. Wang, X.-Z. Yuan, J.J. Martin, D. Yang, J. Qiao, et al., A review on water balance in the membrane electrode assembly of proton exchange membrane fuel cells, Int. J. Hydrog. Energy 34 (2009) 9461–9478.
[66] L. Treutlein, A. Javed, N.L. Wolf, H. Kungl, A. Karl, E. Jodat, et al., Gas Crossover in Membrane Electrolyzers—The Impact of MEA Conditioning on Gas Permeability, J. Electrochem. Soc. 172 (2025) 064507.
[67] A. Chowdhury, C.J. Radke, A.Z. Weber, Transport Resistances in Fuel-Cell Catalyst Layers, ECS Trans. 80 (2017) 321.
[68] X. Li, X. Cai, R. Lin, Study on the Regulation of the Three-Phase Microenvironment in Low-Platinum MEA, SAE Technical Paper, WCX SAE World Congress Experience, 2026.
[69] R. Hong, L. Xing, N. Wang, L. Meng, L. Du, S. Ye, Ionomers: Behind-the-Scenes Influencer Determining the Performance of Membrane Electrode Assemblies in PEM Fuel Cells/Electrolyzers, ACS Energy Letters 11 (2) (2026) 1193–1207.
[70] A. Katzenberg, A. Chowdhury, M. Fang, A.Z. Weber, Y. Okamoto, A. Kusoglu, et al., Highly Permeable Perfluorinated Sulfonic Acid Ionomers for Improved Electrochemical Devices: Insights into Structure–Property Relationships, J. Am. Chem. Soc. 142 (2020) 3742–3752.
[71] D. Yoo, S. Park, S. Oh, J.S. Lee, S. Jung, K. Park, Degradation analysis of ionomer binder using distribution of relaxation times after electrochemical degradation in polymer electrolyte membrane fuel cell, J. Power Sources 663 (2026) 238833.
[72] S. Fang, G. Liu, M. Li, H. Zhang, J. Yu, F. Zhang, et al., Tailoring Ionomer Chemistry for Improved Oxygen Transport in the Cathode Catalyst Layer of Proton Exchange Membrane Fuel Cells, ACS Appl. Energy Mater. 6 (2023) 3590–3598.

[73] J. Lim, D. Kim, S.-D. Yim, Y.-J. Sohn, S.G. Lee, Effects of ionomer chemistry on nanostructure and reactant transport properties in high oxygen permeability ionomers: Molecular dynamics simulation study, J. Power Sources 654 (2025) 237810.
[74] Y. Zou, K. Miyatake, F. Liu, L. Guo, C.Y. Wong, A. Mohamed Ahmed Mahmoud, et al., Highly gas permeable proton-conducting ionomers containing cyclohexyl groups: synthesis, properties, and applications in fuel cell electrodes, Macromolecules 57 (2024) 9833–9840.
[75] A.Z. Weber, A. Kusoglu, Unexplained transport resistances for low-loaded fuel-cell catalyst layers, J. Mater. Chem. A 2 (2014) 17207–17211.
[76] M.K. Debe, Electrocatalyst approaches and challenges for automotive fuel cells, Nature 486 (2012) 43–51.
[77] M. Liu, H. Hu, Y. Kong, I.Z. Montiel, V. Kolivoška, A.V. Rudnev, et al., The role of ionomers in the electrolyte management of zero-gap MEA-based CO2 electrolysers: A Fumion vs, Nafion comparison. Appl. Catal. B. 335 (2023) 122885.
[78] M.N. Idros, Y. Wu, T. Duignan, M. Li, H. Cartmill, I. Maglaya, et al., Effect of dispersing solvents for an ionomer on the performance of copper catalyst layers for CO2 electrolysis to multicarbon products, ACS Appl. Mater. Interfaces 15 (2023) 52461–52472.
[79] S. Quesada, L. Gatti, M. Alberghini, A. Tommasi, M. Etzi, A. Mezza, et al., A deeper understanding of flooding dynamics in gas diffusion electrodes for CO2 electrolyzer: how interfacial pressure shapes gas–liquid stability, Chem. Eng. J. 171393 (2025).
[80] M.E. Leonard, L.E. Clarke, A. Forner-Cuenca, S.M. Brown, F.R. Brushett, Investigating electrode flooding in a flowing electrolyte, gas-fed carbon dioxide electrolyzer, ChemSusChem 13 (2020) 400–411.
[81] M. Etzi, J. Dangbegnon, A. Chiodoni, C.F. Pirri, Impact of gas diffusion layer architecture on the performances of Cu-based electrodes for CO2 electroreduction to ethylene in flow reactors, J. CO_2 Util. 83 (2024) 102772.
[82] J.K. Dangbegnon, M. Etzi, J. Zeng, A. Chiodoni, C.F. Pirri, CO 2 electroreduction towards ethylene on copper phosphate-derived catalysts in alkaline flow cell, Catal. Sci. Technol. 15 (2025) 2318–2326.
[83] Y. Nagao, Proton-conducting polymers: key to next-generation fuel cells, electrolyzers, batteries, actuators, and sensors, ChemElectroChem 11 (2024) e202300846.
[84] M. Mandal, M. Moore, M. Secanell, Measurement of the protonic and electronic conductivities of PEM water electrolyzer electrodes, ACS Appl. Mater. Interfaces 12 (2020) 49549–49562.
[85] M.S. Wilson, S. Gottesfeld, Thin-film catalyst layers for polymer electrolyte fuel cell electrodes, J. Appl. Electrochem. 22 (1992) 1–7.
[86] C. Gerling, M. Hanauer, U. Berner, Friedrich K. Andreas, Full factorial in situ characterization of ionomer properties in differential PEM fuel cells, J. Electrochem. Soc. 168 (2021) 084504.
[87] V. Atanasov, A. Oleynikov, J. Xia, S. Lyonnard, J. Kerres, Phosphonic acid functionalized poly (pentafluorostyrene) as polyelectrolyte membrane for fuel cell application, J. Power Sources 343 (2017) 364–372.
[88] V. Atanasov, A.S. Lee, E.J. Park, S. Maurya, E.D. Baca, C. Fujimoto, et al., Synergistically integrated phosphonated poly (pentafluorostyrene) for fuel cells, Nat. Mater. 20 (2021) 370–377.
[89] J. Jung, K.H. Lim, S. Maurya, L.D. Manriquez, V. Atanasov, C.-H. Ahn, et al., Dispersing agents impact performance of protonated phosphonic acid high-temperature polymer electrolyte membrane fuel cells, ACS Energy Lett. 7 (2022) 1642–1647.
[90] R. Shimizu, Y.-C. Park, K. Kakinuma, A. Iiyama, M. Uchida, Effects of both oxygen permeability and ion exchange capacity for cathode ionomers on the performance and durability of polymer electrolyte fuel cells, J. Electrochem. Soc. 165 (2018). F3063-F71.
[91] Y. Sun, X. Zhang, C. Wang, X. Bai, L. Fan, J. Fan, et al., Effect of poly (3, 4-ethylenedioxythiophene): poly (styrenesulfonate) on low-iridium catalyst layer for proton exchange membrane water electrolysis, J. Power Sources 586 (2023) 233678.
[92] S. Byun, J.-H. Yu, J. Choi, S. Yun, Y. Roh, C.B. Dzakpasu, et al., Unraveling the cohesive and interfacial adhesive strengths of electrodes for automotive fuel cells, J. Power Sources 455 (2020) 227928.
[93] M. Chen, M. Mandal, K. Groenhout, G. McCool, H.M. Tee, B. Zulevi, et al., Self-adhesive ionomers for durable low-temperature anion exchange membrane electrolysis, J. Power Sources 536 (2022) 231495.
[94] V.D.C. Tinh, D. Kim, Enhancement of oxidative stability of PEM fuel cell by introduction of HO• radical scavenger in Nafion ionomer, J. Membr. Sci. 613 (2020) 118517.
[95] S. Yuk, J. Jung, K.-Y. Song, D.W. Lee, D.-H. Lee, S. Choi, et al., Addressing the detrimental effect of CeO2 radical scavenger on the durability of polymer electrolyte membrane fuel cells, Chem. Eng. J. 452 (2023) 139061.
[96] O. Špalek, J. Balej, I. Paseka, Kinetics of the decomposition of hydrogen peroxide in alkaline solutions, Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases 78 (1982), 2349-59.
[97] V. Russo, L. Protasova, R. Turco, M. De Croon, V. Hessel, E. Santacesaria, Hydrogen peroxide decomposition on manganese oxide supported catalyst: from batch reactor to continuous microreactor, Ind. Eng. Chem. Res. 52 (2013), 7668-76.
[98] C.G. Arges, L. Zhang, Anion exchange membranes' evolution toward high hydroxide ion conductivity and alkaline resiliency, ACS Appl. Energy Mater. 1 (2018) 2991–3012.
[99] Y. Zhang, J. Parrondo, S. Sankarasubramanian, V. Ramani, Detection of reactive oxygen species in anion exchange membrane fuel cells using in situ fluorescence spectroscopy, ChemSusChem 10 (2017) 3056–3062.
[100] J.G. Petrovick, D.I. Kushner, P. Goyal, A. Kusoglu, C.J. Radke, A.Z. Weber, Electrochemical measurement of water transport numbers in anion-exchange membranes, J. Electrochem. Soc. 170 (2023) 114519.
[101] K.M. Hugar, H.A.I.V. Kostalik, G.W. Coates, Imidazolium Cations with Exceptional Alkaline Stability: A Systematic Study of Structure–Stability Relationships, J. Am. Chem. Soc. 137 (2015) 8730–8737.
[102] M. Marino, K. Kreuer, Alkaline stability of quaternary ammonium cations for alkaline fuel cell membranes and ionic liquids, ChemSusChem 8 (2015) 513–523.
[103] S. Gu, R. Cai, T. Luo, Z. Chen, M. Sun, Y. Liu, et al., A soluble and highly conductive ionomer for high-performance hydroxide exchange membrane fuel cells, Angew. Chem. Int. Ed. 48 (2009) 6499–6502.
[104] X. Wang, J. Pan, A. Zhu, Y. Hong, X. Zhao, Q. Zhang, N-doped Carbon Additives in the Anode Catalyst Layer for Improved Pore Structure and Water Management of Anion Exchange Membrane Fuel Cells, Small 21 (2025) e08063.
[105] P.O.G. Ferreira, Y. Shao-Horn, D. Morgan, R. Makharia, S. Kocha, et al., Instability of Pt/ C electrocatalysts in proton exchange membrane fuel cells: a mechanistic investigation. Journal of The Electrochemical, Society 152 (2005). A2256-A71.
[106] A. Kongkanand, M.F. Mathias, The priority and challenge of high-power performance of low-platinum proton-exchange membrane fuel cells, J. Phys. Chem. Lett. 7 (2016) 1127–1137.
[107] H. Ogasawara, Y. Sawatari, J. Inukai, M. Ito, Adsorption of bisulfate anion on a Pt (111) electrode: a comparison of in-situ and ex-situ IRAS, J. Electroanal. Chem. 358 (1993) 337–342.
[108] H. Yano, T. Uematsu, J. Omura, M. Watanabe, H. Uchida, Effect of adsorption of sulfate anions on the activities for oxygen reduction reaction on Nafion®-coated Pt/carbon black catalysts at practical temperatures, J. Electroanal. Chem. 747 (2015) 91–96.
[109] V. Briega-Martos, T. Fuchs, J. Drnec, O.M. Magnussen, S. Cherevko, Effects of anions and surface structure on Pt single crystal dissolution in acidic electrolytes, ChemElectroChem 11 (2024) e202300554.
[110] K.J. Mayrhofer, J.C. Meier, S.J. Ashton, G.K. Wiberg, F. Kraus, M. Hanzlik, et al., Fuel cell catalyst degradation on the nanoscale, Electrochem. Commun. 10 (2008) 1144–1147.
[111] D. Li, H.T. Chung, S. Maurya, I. Matanovic, Y.S. Kim, Impact of ionomer adsorption on alkaline hydrogen oxidation activity and fuel cell performance, Curr. Opin. Electrochem. 12 (2018) 189–195.
[112] I. Matanovic, S. Maurya, E.J. Park, J.Y. Jeon, C. Bae, Y.S. Kim, Adsorption of polyaromatic backbone impacts the performance of anion exchange membrane fuel cells, Chem. Mater. 31 (2019) 4195–4204.
[113] D. Li, A.R. Motz, C. Bae, C. Fujimoto, G. Yang, F.-Y. Zhang, et al., Durability of anion exchange membrane water electrolyzers, Energy Environ. Sci. 14 (2021) 3393–3419.
[114] D. Li, I. Matanovic, A.S. Lee, E.J. Park, C. Fujimoto, H.T. Chung, et al., Phenyl oxidation impacts the durability of alkaline membrane water electrolyzer, ACS Appl. Mater. Interfaces 11 (2019) 9696–9701.
[115] P.M. Budd, S.M. Makhseed, B.S. Ghanem, K.J. Msayib, C.E. Tattershall, N. B. McKeown, Microporous polymeric materials. materials today. 7 (2004) 40–46.
[116] C. Astorino, E. De Nardo, S. Lettieri, G. Ferraro, M. Bartoli, M. Etzi, et al., Investigation of Solid-State Thermal Decomposition of Ammonia Borane Mix with Sulphonated Poly(ellagic Acid) for Hydrogen Release, Polymers 16 (2024).
[117] M. Gede, G. Ignacz, C.S.P. De Castro, B. Dereli, M. Ferree, F. Laquai, et al., Tailoring polymers of intrinsic microporosity as photoredox catalysts for continuous-flow reaction–separation processes, Nat. Commun. 17 (2026) 7062.
[118] J. Ying, Z. Cui, L. Tu, T. Liu, S. Lu, Q. Shen, et al., Polymers with intrinsic microporosity engineered via acid-base pairs for highly selective lithium-ion transport channels, J. Membr. Sci. 741 (2026) 125059.
[119] M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, et al., Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), Pure Appl. Chem. 87 (2015) 1051–1069.
[120] N.B. McKeown, Polymers of intrinsic microporosity (PIMs), Polymer 202 (2020) 122736.
[121] B. Qiu, Y. Gao, P. Gorgojo, X. Fan, Membranes of polymer of intrinsic microporosity PIM-1 for gas separation: modification strategies and meta-analysis, Nano-Micro Lett. 17 (2025) 114.
[122] W.H. Lee, J.G. Seong, X. Hu, Y.M. Lee, Recent progress in microporous polymers from thermally rearranged polymers and polymers of intrinsic microporosity for membrane gas separation: Pushing performance limits and revisiting trade-off lines, J. Polym. Sci. 58 (2020) 2450–2466.
[123] T. Joo, K. Mizrahi Rodriguez, H. Lee, D. Acharya, C.M. Doherty, Z.P. Smith, The role of free volume, hydrogen bonds, and crosslinks on physical aging in polymers of intrinsic microporosity (PIMs), J. Mater. Chem. A 11 (2023) 15943–15957.
[124] F. Begni, E. Lasseuguette, G. Paul, C. Bisio, L. Marchese, G. Gatti, et al., Hyper Cross-Linked Polymers as Additives for Preventing Aging of PIM-1 Membranes, Membranes 11 (2021) 463.
[125] A. Ayyaz, A.B. Foster, L. Cseri, G. Szekely, P.M. Budd, Greener Synthesis of the Polymer of Intrinsic Microporosity PIM-1 for Gas Separation, ACS Sustain. Chem. Eng. 13 (2024) 2784–2792.
[126] X. Sun, J. Guan, X. Wang, X. Li, J. Zheng, S. Li, et al., Phosphonated Ionomers of Intrinsic Microporosity with Partially Ordered Structure for High-Temperature Proton Exchange Membrane Fuel Cells, ACS Central Sci. 9 (2023) 733–741.
[127] F. Kurul, B. Doruk, S.N. Topkaya, Principles of green chemistry: building a sustainable future, Discover Chem. 2 (2025) 68.

[128] M. Azevedo Beluomini, N. Ramos Stradiotto, M.V. Boldrin Zanoni, M. Carta, N. B. McKeown, P.J. Fletcher, et al., Triphasic Oxygen Storage in Wet Nanoparticulate Polymer of Intrinsic Microporosity (PIM-1) on Platinum: An Electrochemical Investigation, ACS Appl. Mater. Interfaces 16 (2024) 37865–37873.
[129] J. Choi, M.-H. Kim, J.Y. Han, J.E. Chae, W.H. Lee, Y.M. Lee, et al., Application of spirobiindane-based microporous poly (ether sulfone) s as polymeric binder on solid alkaline exchange membrane fuel cells, J. Membr. Sci. 568 (2018) 67–75.
[130] J.E. Chae, B.H. Kim, J.H. Noh, J. Jung, J.-Y. Kim, J.H. Jang, et al., Effect of the spirobiindane group in sulfonated poly (arylene ether sulfone) copolymer as electrode binder for polymer electrolyte membrane fuel cells, J. Ind. Eng. Chem. 47 (2017) 315–322.
[131] R. Haider, Y. Wen, Z.-F. Ma, D.P. Wilkinson, L. Zhang, X. Yuan, et al., High temperature proton exchange membrane fuel cells: progress in advanced materials and key technologies, Chem. Soc. Rev. 50 (2021) 1138–1187.
[132] N. Chen, C. Hu, H.H. Wang, S.P. Kim, H.M. Kim, W.H. Lee, et al., Poly (alkyl-terphenyl piperidinium) ionomers and membranes with an outstanding alkaline-membrane fuel-cell performance of 2.58 W cm− 2, Angew. Chem. Int. Ed. 60 (2021) 7710–7718.
[133] H. Tang, K. Geng, D. Aili, Q. Ju, J. Pan, G. Chao, et al., Low Pt loading for high-performance fuel cell electrodes enabled by hydrogen-bonding microporous polymer binders, Nat. Commun. 13 (2022) 7577.
[134] W.H. Doh, L. Gregoratti, M. Amati, S. Zafeiratos, Y.T. Law, S.G. Neophytides, et al., Scanning Photoelectron Microscopy Study of the Pt/Phosphoric-Acid-Imbibed Membrane Interface under Polarization, ChemElectroChem 1 (2014) 180–186.
[135] M. Prokop, T. Bystron, K. Bouzek, Electrochemistry of phosphorous and hypophosphorous acid on a Pt electrode, Electrochim. Acta 160 (2015) 214–218.
[136] S. Kaserer, K.M. Caldwell, D.E. Ramaker, C. Roth, Analyzing the influence of H3PO4 as catalyst poison in high temperature PEM fuel cells using in-operando X-ray absorption spectroscopy, J. Phys. Chem. C 117 (2013) 6210–6217.
[137] Q. He, B. Shyam, M. Nishijima, D. Ramaker, S. Mukerjee, Mitigating phosphate anion poisoning of cathodic Pt/C catalysts in phosphoric acid fuel cells, J. Phys. Chem. C 117 (2013) 4877–4887.
[138] D. Aili, D. Henkensmeier, S. Martin, B. Singh, Y. Hu, J.O. Jensen, et al., Polybenzimidazole-based high-temperature polymer electrolyte membrane fuel cells: new insights and recent progress, Electrochem. Energy Rev. 3 (2020) 793–845.
[139] J. Park, K. Kwon, M. Cho, S.-G. Hong, T. Kim, D. Yoo, Role of binders in high temperature PEMFC electrode, J. Electrochem. Soc. 158 (2011). B675-B81.
[140] S. Dey, M. Aggarwal, D. Chakraborty, P.S. Mukherjee, Uncovering tetrazoles as building blocks for constructing discrete and polymeric assemblies, Chem. Commun. 60 (2024) 5573–5585.
[141] A. Modestov, M. Tarasevich, V.Y. Filimonov, A.Y. Leykin, Influence of catalyst layer binder on catalyst utilization and performance of fuel cell with polybenzimidazole-H3PO4 membrane, J. Electrochem. Soc. 156 (2009). B650-B6.
[142] J. Jung, J. Ku, Y.S. Park, C.-H. Ahn, J.-H. Lee, S.S. Hwang, et al., Advances in ion conducting membranes and binders for high temperature polymer electrolyte membrane fuel cells, Polym. Rev. 62 (2022) 789–825.
[143] M. Burba, E. Pargoletti, F. Marken, N.B. McKeown, M. Carta, A. Vertova, et al., Polymer of Intrinsic Microporosity as Binders for both Acidic and Alkaline Oxygen Reduction Electrocatalysis, ChemElectroChem 11 (2024) e202300481.
[144] B.G. Kim, D. Henkensmeier, H.-J. Kim, J.H. Jang, S.W. Nam, T.-H. Lim, Sulfonation of PIM-1—towards highly oxygen permeable binders for fuel cell application, Macromol. Res. 22 (2014) 92–98.
[145] S. Yang, H. Li, W. Zou, R. Ling, X. Ma, S. Chen, et al., Sulfonated Microporous Polyxanthene Binder for High-Temperature Hydrogen Fuel Cells, JACS Au 4 (2024) 3277–3283.
[146] H. Khalid, M. Plevová, T.T. Bui, M. Najibah, J. Hnát, K. Bouzek, et al., Microporous Electrode Binders for Anion Exchange Membrane Water Electrolyzers, Small 20 (2024) 2401592.
[147] X. Wang, L. Liu, N. Li, Novel intrinsic microporous binders in the cathode catalyst layer for high-performance alkaline water electrolysis, J. Power Sources 641 (2025) 236916.
[148] S.C. Perry, S.M. Gateman, R. Malpass-Evans, N. McKeown, M. Wegener, P. Nazarovs, et al., Polymers with intrinsic microporosity (PIMs) for targeted CO2 reduction to ethylene, Chemosphere 248 (2020) 125993.
[149] E. Madrid, J.P. Lowe, K.J. Msayib, N.B. McKeown, Q. Song, G.A. Attard, et al., Triphasic Nature of Polymers of Intrinsic Microporosity Induces Storage and Catalysis Effects in Hydrogen and Oxygen Reactivity at Electrode Surfaces, ChemElectroChem 6 (2019) 252–259.