Fully Hydrocarbon Membrane Electrode Assemblies for Proton Exchange Membrane Fuel Cells and Electrolyzers: An Engineering Perspective

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1. Introduction

Electrochemical energy converters based on proton-exchange membranes (PEMs) are considered as the key technology to tackle global warming on a short-term time scale. PEM-based electrochemical devices rely on proton-conducting polymers – which until today are based on sulfonated perfluorosulfonic acids (PFSAs). Since the introduction in 1969, PFSA-based ionomers are largely dominating the market due to their unbeaten properties. Although the limitations of PFSAs are known in literature,[1,2] no reasonable alternative was reported until recent years. By using mechanical or chemical reinforcements, it was possible to keep PFSAs as material of choice for the current generation of electrochemical energy converters and achieve even the ambitious energy converters and achieve high efficiency and operating potential, lower Ohmic and mass transport losses, and finally a higher operation temperature. A recent modeling study of Toyota revealed the remarkable gap between the current state of the art and the ultimate performance goals for fuel cells (Figure 1).

To achieve these very ambitious goals, some “early stage” materials were combined to estimate a polarization curve (dashed green line) that theoretically can exceed the 2030 target value (solid green line). Those materials include increased catalytic active sites and intrinsic activity[5,6] and catalyst layers with mesoporous Pt/C from GM R&D.[7] The optimal electrode ionomer should provide high proton conductivity at high temperatures (>100 °C) and low humidity (<50% relative humidity (RH)), thus high ion exchange capacity (IEC)[8] without poisoning the catalyst[9,10] and finally a high oxygen permeability.[11,12] The gas diffusion layers should also be improved to significantly reduce the gas transport losses.[13]

The desired high operating temperatures (>100 °C) are a bottleneck for state-of-the-art PFSA membrane-electrode assemblies (MEAs), while being highly attractive to boost efficiency, increase cooling gradients, and increase CO tolerance. The low glass transition temperatures of conventional PFSAs[14] complicate cell operation above ~110 °C, which is below the ultimate targets between 120 or even 150 °C. In addition to temperature limitations and gas crossover requirements, significantly higher proton conductivity as well as lower costs are demanded to fulfill the mid-term development goals. Based on those projections, it is striking that those targets might not be met with PFSA-based materials and novel, more proton conductive and temperature stable ionomers need to be developed.
As for fuel cells, the search for novel ionomer materials for PEM water electrolyzers (WEs) is still ongoing. 2050 targets for operation at 80 °C operation temperature, >70 bar cell pressure, a lifetime of 100 000–120 000 h, and a hydrogen purity of 99.9–99.9999% challenge the material development since also the hydrogen price needs to be reduced\(^{[15]}\) as low as 1 $ kg\(^{-1}\) until 2030, as recently introduced by DOE.\(^{[26]}\) Current state of the art in electrolyzers are relatively thick PFSA membranes (e.g., 180 µm Nafion N117, or 120 µm Nafion N115). The protonic resistance of these thick membranes is relatively high (>100 mΩ cm\(^2\)). Utilizing thinner membranes would increase the voltage efficiency,\(^{[15]}\) but thin membranes would not meet the high durability requirements of electrolyzers. In addition, thin membranes have a higher gas crossover, which decreases the Faradaic efficiency and boosts degradation, while also posing a safety hazard. Thus, ionomers need to be developed, which combine high proton conductivity, low gas crossover, and meet the stability requirements. As in fuel cells, hydrocarbon-based ionomers bear the potential to meet all these requirements, while being more cost-efficient and environmentally benign as PFSA.

The goal of this work is to provide an overview on the current state of performance and stability of the latest hydrocarbon MEAs for fuel cells and electrolyzers, where most relevant reports were published achieving performances and durability data comparable to PFSA baselines. In addition, we compare and list possible similarities and challenges arising from a shift from PFSA to hydrocarbon ionomers when it comes to MEA fabrication, conditioning, and operation under various conditions. Finally, we try to provide an outlook on the remaining challenges and important directions for future research in hydrocarbon MEA development.

### 2. State of the Art of Hydrocarbon MEAs

In the recent years, several research groups worldwide suggested novel, mostly phenylene-based hydrocarbon ionomers which showed for the first time competitive performance and preliminary degradation stability compared to their PFSA equivalents.\(^{[17–19]}\) The readers interested in the polymer chemistry perspective of hydrocarbon ionomers and membranes are directed to the review articles of Zhang and Shen,\(^{[20]}\) Adhikari et al.,\(^{[21]}\) Shin et al.,\(^{[22]}\) Park et al.,\(^{[2]}\) Byun et al.,\(^{[23]}\) Kim,\(^{[2]}\) and Adamski et al.\(^{[24]}\) The review of Zhang and Shen\(^{[20]}\) covers the properties, applications, and synthesis strategies for various proton exchange membranes, i.e., PFSA-based, partially fluorinated acid ionomer membrane, nonfluorinated acid ionomer membrane, etc. The review of Adhikari et al.\(^{[21]}\) also covers developments of both fluorinated and nonfluorinated ionomers, but with emphasis on chemical and mechanical stability and performance in electrochemical applications. Recent works on developments of various chemical structures, engineering the morphology and architecture of hydrocarbon-based proton-exchange membranes are addressed in the in-depth review articles of Shin et al.\(^{[22]}\) The review articles of Park et al.\(^{[2]}\) and Byun et al.\(^{[23]}\) also focused on recent developments of hydrocarbon-based ionomer, but with a focus on long-term performance of fuel cells in medium temperature and/or low humidity to substitute fluorinated proton exchange membrane in fuel cells. Finally, to tackle tough scientific challenges in fuel cells and electrolyzers, Kim\(^{[2]}\) discussed synthetic approaches, performance, challenges, and prospects of ionomers with high ionic concentrations (>1.2 meq g\(^{-1}\)) in the interesting review. The evolution of sulfonated polyphenylene as proton exchange membrane for fuel cells was summarized further in the recent published review article by Adamski et al.\(^{[24]}\) In the following sections, the main approaches in the development of hydrocarbon-based ionomers and their respective properties in the device are briefly summarized with focus on engineering properties in the membrane-electrode assembly.

#### 2.1. Fuel Cells

##### 2.1.1. Hydrocarbon Ionomers as Membrane

In general, the desired properties for fuel cell membranes are higher chemical stability and proton conductivity while maintaining mechanical integrity. In PFSA electrolytes, the hydrophobic, polytetrafluoroethylene (PTFE)-like backbone separates strongly from hydrophilic, sulfonated side chains due to the extreme difference in polarity within the ionomer.\(^{[14,25]}\) In the wet state, the hydrophilic groups absorb water and create a percolating domain for proton transport, while the hydrophobic domains provide mechanical stability and integrity of the polymer.\(^{[14,25]}\)

Hydrocarbon-based ionomers for electrochemical applications are usually based on polyphenylene-\(^{[18,19,24,26–28]}\) polyphenylene sulfonyl-\(^{[29,30]}\) poly(arylene ether sulfonyl)-\(^{[31,32]}\) based backbones and numerous derivatives thereof have shown to be susceptible to chemical degradation. Due to the lower density of polyaromatic hydrocarbon (>1.2 g cm\(^{-3}\))\(^{[13,34]}\) compared to that of PFSA counterparts (>2 g cm\(^{-3}\)),\(^{[14]}\) hydrocarbon-based ionomers typically require a significantly higher amount of acid functional groups per repeating unit to achieve similar proton conductivity to PFSA, which results in a higher gravimetric IEC (≥2 meq g\(^{-1}\)).\(^{[8,24]}\) The less expressed hydrophobic/hydrophilic phase separation in hydrocarbon ionomers leads to narrower, less connected domains for proton conduction, and higher swelling under wet conditions.\(^{[25]}\) To maintain mechanical integrity for practical use, swelling must be reduced. Hence, an appropriate design for hydrocarbon ionomers is very important. Common approaches to modify the structural
properties of ionomers are block copolymerization, branched copolymerization, and graft copolymerization. Several reports describe that block copolymers have a higher proton conductivity than random copolymer with similar IECs – even under low humidity.\cite{35,36} Increasing the density of the sulfonate groups in the hydrophilic moieties of the ionomer (Figure 2c) has also shown to be advantageous.\cite{33,37} Han et al.\cite{38} recently observed a lower through-plane proton conductivity of a multiblock membrane (biphenol-based sulfonated poly(arylene ether sulfone) – BPSH) compared to a random analog in water electrolyzers. The authors suspected that the anisotropic ion conduction behavior of the multiblock BPSH membranes leads to their lower through-plane conductivity.

Besides the architecture of the ionomers, the structure–morphology–properties relationships of the membranes are also affected by the processing. Membranes are usually formed by casting from a solution/dispersion. Hence, apart from ionomer structures, the solvent composition, drying temperature, and solvent removal rate also influence the membrane properties. Post-treatments to modify the morphology are thermal annealing,\cite{40} solvent-vapor-annealed deposition,\cite{41} surface modification by atmospheric plasma treatment,\cite{42} elastomeric mold method to fabricate micropatterned membranes,\cite{43} pressing, applying shear- and electrical field aligning,\cite{44} polymer blends and/or cross-linking.\cite{45,46} To improve the mechanical and chemical stability, promising approaches from PFSA-based systems were adopted for hydrocarbon-based membranes. For instance, integrating inert substrates,\cite{47,48} hydroxyl radical scavengers (e.g., CeO$_2$ nanoparticles),\cite{49,50} or nanofibers.\cite{51} These approaches are discussed further in detail in Section 3.1.

2.1.2. Hydrocarbon Ionomers as Electrode Electrolyte

MEAs with hydrocarbon-based membranes and Nafion electrodes suffer frequently from delamination. This is mainly due to poor adhesion and differences in dimensional swelling between hydrocarbon-based and PFSA ionomers.\cite{52} Applying hydrocarbon-based ionomers as electrode electrolyte in MEAs with hydrocarbon membranes not only improves the membrane/catalyst interface and proton conductive network, but also facilitates the Pt recovery process. The need to handle the highly toxic and corrosive hydrogen fluoride is thereby avoided. The feasibility of hydrocarbon ionomers in catalyst layers was summarized in a review article by Peron et al.,\cite{1} stating the need for novel hydrocarbon ionomers that mimic the PFSA-typical phase-separated structure of hydrophobic/hydrophilic domains in the catalyst layer (CL) ionomer.

Figure 3 summarizes the development progress of fully hydrocarbon MEAs since 2008. All studies on fully hydrocarbon
MEAs in literature until 2021 demonstrate the suitability of hydrocarbon ionomers developed for membranes also in the catalyst layer. The studies adopted the approaches of optimizing the PFSA catalyst layers, e.g., by adjusting the ionomer/carbon (I/C) ratio\textsuperscript{[17,53]} or the solvent systems,\textsuperscript{[54,55]} adding additives,\textsuperscript{[56,57]} and optimizing the IEC/degree of sulfonation\textsuperscript{[33,58]} and the molecular weight (MW).\textsuperscript{[11]} The first proof of performances, approaching the PFSA state of the art (>2 W cm\textsuperscript{−2} in \textit{H}_2/O\textsubscript{2} and >1 W cm\textsuperscript{−2} in \textit{H}_2/air operation) was reported in 2021 by Nguyen et \textit{al.}\textsuperscript{[59]} using thin Pemion membranes and PtCo/C cathode catalyst layers with optimized I/C ratio and ink solvent composition.

It is remarkable that most of the studies in literature optimized the MEAs for high to fully humidified conditions (>75% RH), while in automotive or heavy-duty applications, usually low RH is desired. In addition to Figure 3, Table 1 summarizes available data of MEAs with different membrane materials, ink compositions, as well as the performance under \textit{H}_2/O\textsubscript{2} and \textit{H}_2/air, all under fully humidified gas feeds.

To improve the performance of a given ionomer type and catalyst, it is essential to first optimize the ionomer content in the catalyst layer for the desired operating conditions and simultaneously find the right solvent system for the catalyst ink. The important role of ionomer content in the catalyst layer and solvents of catalyst inks are reported immensely in literature.\textsuperscript{[07,53,62–67]} The following paragraphs give a brief overview on these studies.

**The Role of the Ionomer Content in Catalyst Layers:** Similar to catalyst layers with PFSA ionomer, there is also an optimum ionomer content for hydrocarbon-based catalyst layers. Below the optimal ionomer content, losses due to high proton resistances are significant.\textsuperscript{[17,53,68,69]} In general, significantly lower amounts of hydrocarbon ionomer (<15 wt%) compared to PFSAs (>20–30 wt%) were found to enable to achieve the highest performance.\textsuperscript{[1,17,53,59]} This is explained by the much higher gravimetric IEC of hydrocarbon-based ionomers (typically > 2 meq g\textsuperscript{−1})\textsuperscript{[8,24]} compared to that of PFSA (≈1 meq g\textsuperscript{−1}) to achieve similar proton conductivity, as previously mentioned. A higher gravimetric IEC imparts increased hydrophilicity, and as a result, potentially excessive water sorption, swelling, and flooding, when fully hydrated.\textsuperscript{[59]} Given the different densities of both material classes, the optimal ionomer volume fractions in the electrode are similar for both material classes, i.e., in the range of 15 vol%. Liu \textit{et al.}\textsuperscript{[68]} proposed in their study that at

| Table 1. Summary of fabrication and performance of hydrocarbon-based fuel cell MEAs since the 2010s. |

| Ref. Year | Catalyst ink solvent MEA fabrication method | MEA parameters | Performance characterization |
|-----------|---------------------------------------------|----------------|------------------------------|
| \[32\] 2012 | NMP\textsuperscript{a} + IPA\textsuperscript{a} + H\textsubscript{2}O | Doctor blading 0.4 | Pt(C, 40 wt%) | SPAES\textsuperscript{b} | 0.2 |
| \[55\] 2013 | MeOH + H\textsubscript{2}O | Spray coating 0.4 | Pt/C, 46 wt% | sPP\textsuperscript{d} | 0.2 |
| \[33\] 2018 | MeOH + H\textsubscript{2}O | Spray coating 0.4 | Pt/C, 46 wt% | sPPP\textsuperscript{d} | 0.2 |
| \[17\] 2020 | MeOH + H\textsubscript{2}O | Spray coating 0.4 | Pt/C, n/a | sPPB\textsuperscript{d} | 0.2 |

\(\textsuperscript{a}\)N-Methyl-2-pyrrolidone; \(\textsuperscript{b}\)Isopropyl alcohol; \(\textsuperscript{c}\)Sulfonated poly(arylene ether sulfone); \(\textsuperscript{d}\)Sulfophenylene; \(\textsuperscript{e}\)Sulfonated phenylated poly(phenylene); \(\textsuperscript{f}\)Biphenyl-linked sulfophenylated poly(phenylene).

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least 13 vol% ionomer in the catalyst layer is required for a well-connected ionomer phase within a wide range of humidity to avoid significant proton resistance. Above the optimal ionomer content, the pore volume is reduced.\cite{76} A reduced pore volume impedes the oxygen and water transport, also deteriorates the fuel cell performance in particular at high current densities.\cite{77} Overall, independent on the material classes, the ideal ionomer content in the electrode is the delicate balance between sufficient ionomer volume fraction for good proton transport and the maximum possible pore volumes for gas transport.

**The Role of the Catalyst Ink Solvent System:** To optimize the performance of fully hydrocarbon fuel cells, the solvent system of the catalyst ink plays an important role. For instance, Strong et al.\cite{55} compared the performance of catalyst layers for inks composed of sulfonated poly(arylene ether sulfone) (SPAES) ionomer (IEC $2.21 \text{ meq g}^{-1}$) in MeOH and water (1:1 v/v) to that composed of the same ionomer solution, but with an additional amount of dimethylformamide (0.38 wt% of the catalyst ink). The authors observed an overall decrease in performance, which was accounted to a reduced electrochemical active surface area (ECSA), proton conductivity, and porosity\cite{55}. They proposed to develop hydrocarbon ionomers that are dissolvable in low boiling point solvents. Recently, Balogun et al.\cite{62} investigated the effects of catalyst inks with low boiling point solvents (methanol, ethanol, isopropanol) and water (alcohol:water = 3:1 w/w) on the pore volume and the fuel cell polarization curves. The authors observed that highest performance is achieved with the methanol-based ink, based on the ratio of 3:1 w/w alcohol:water mixtures. According to the porosimetry data, the higher performance is related to the higher total pore volume of the methanol-based catalyst layer (0.56 cm$^3$ g$^{-1}_{carbon}$) compared to that of the isopropanol-based catalyst layer (0.39 cm$^3$ g$^{-1}_{carbon}$). The study confirms the critical role of the alcohol property on the catalyst layer structure and the fuel cell performance, as was observed in PFSA-based fuel cells.\cite{85,66} The changes in performance due to solvent systems for PFSA are typically attributed to different aggregation states of the ionomer which have a direct impact on the local oxygen transport.\cite{67,71} Furthermore, PFSA are typically dispersed as colloidal aggregates in alcoholic mixtures that form a percolated network without covering and isolating all of the carbon support. Hydrocarbon ionomers, by contrast, are often dissolved in the mixtures, which ensure uniform distribution but bear the risk of penetrating and blocking primary pore space or electrically isolating parts of the catalyst layer.\cite{1} Thus, extensive studies are required for further understanding of catalyst/ionomer interaction in hydrocarbon-based fuel cells, especially with the presence of aromatic backbones and a high number of sulfonated groups in typical hydrocarbon ionomers.

Further performance improvements can be achieved by, e.g., changing carbon supports in the catalyst layer,\cite{72,73,74} or adding porogens\cite{75,76} or hydrophobic agents\cite{52,79,80} to the catalyst layer. Changing the carbon support can manipulate the ionomer distribution in the catalyst layer, which influences proton conductivity and the mass transport. Adding porogens to the catalyst layer can create a higher volume fraction of voids in the catalyst layer, which can reduce oxygen mass transport and promote water transport.\cite{81,82} Water transport can also be promoted by adding hydrophobic agents into the catalyst layers, as the wetting properties of the catalyst layer are modified thereby. Studies that reported improvements in performance based on these ideas are summarized in the following sections.

**The Role of Carbon Supports:** The carbon support has a great impact on the ionomer distribution in the catalyst layer, which was shown in several studies for PFSA.\cite{72,73} For instance, Soboleva et al.\cite{72} showed that catalyst layers with Ketjenblack have a high water retention as Ketjenblack possesses a broad pore size distribution and a large surface area ($\approx$900 m$^2$ g$^{-1}$). Catalyst layers with Vulcan rather showed a water repelling action due to the lower surface area ($\approx$200 m$^2$ g$^{-1}$) and a narrower pore size distribution than Ketjenblack. Thus, a well-connected proton-conducting network can be formed in Vulcan-based catalyst layers with a low ionomer content, while in Ketjenblack-based catalyst layer, a higher ionomer content is required for a well-connected ionomer network. This is also observed in hydrocarbon-based catalyst layers. The peak power density under fully humidified gas feeds was improved by more than 10% by using Vulcan as catalyst support.\cite{62} The lower surface area of Vulcan enables a sufficient proton conducting network despite the low ionomer content. The low ionomer content promotes the macropore volume\cite{76} which improves the gas transport as discussed in the previous section on the role of the ionomer content. However, at low humidity, a low ionomer content is detrimental for the fuel cell performance, as the proton-conducting network is typically disrupted at low water content.\cite{68,83} The performance in low humidity was not shown in the study with study with bifenyl-linked sulfone-phenylated poly(phenylene) (sPPB)\cite{62} but was discussed in ref. [72]. Thus, under dry conditions, a higher ionomer content in the catalyst layer is desired for a sufficient proton conducting network. However, the ionomer distributes randomly in the catalyst layer, leading to inhomogeneous coverage on catalyst particles.\cite{84} On the other hand, a high ionomer content most likely results in a reduction in macropore volume, leading to higher losses to mass transport. Approaches to mitigate the inhomogeneity of ionomer distribution toward better mass transport will be discussed in Section 3.2.

**The Role of Additives (Porogens and Hydrophobic Agents):** Tailoring the porosity of the catalyst layer (typically between 30% and 60%)\cite{85} is a common approach to improve oxygen and liquid water transport.\cite{86} This interconnected porous network exhibits a bimodal pore-size distribution with primary pores (from 2 to $\approx$50 nm in the carbon particles) and secondary pores (between $\approx$50 and 100 nm between aggregated carbon particles).\cite{87,88} It was shown in several reports, for both PFSA- and hydrocarbon-based catalyst layers, that the addition of porogens (e.g., ammonia oxalate or ZnO,\cite{75} MgO,\cite{76} (bi)carbonates of alkalimetals,\cite{77,78} polyethylene glycol,\cite{57,89} etc.) increases the distribution maximum of secondary pores, which improved the effective oxygen diffusivity and hence, to greater performances. In addition, not only the pore size but also the wetting properties of the carbon support have a significant role on the water transport.\cite{85}

Blending of hydrophobic compounds into catalyst inks has been shown in several reports to improve water management in the cathode. For example, following the approach of tuning the hydrophobicity for PFSA catalyst layers,\cite{79,80} Kim et al.\cite{56} successfully transferred the approach to their wholly hydrocarbon
MEAs and improved the overall performance by ~20%. The MEAs featured 0.6 mg cm\(^{-2}\) additional dimethyl silicone oil (DSO) and SPAES copolymer with “50% degree of sulfonation” (the IEC was not reported). The authors not only observed a decrease in charge transfer, Ohmic, and mass transport resistance with the addition of DSO, but also an increase in the anode outlet humidity. The authors proposed that the facilitated water transport from the cathode to anode side, which leads to an improved overall performance, is attributed to the higher hydrophobicity induced by adding DSO in the cathode catalyst layer.

From the perspective of polymer engineering, analog to the optimization of membrane ionomer, adapting the electrode ionomer to the specific requirements in the electrode is an effective way to improve the performance. Optimizing electrode ionomer can comprise changes in the ion-exchange capacity\(^{[33,58,90]}\) to reduce catalyst poisoning but still maintain the decent proton conductivity in the catalyst layer; or adapting the molecular weight\(^{[31]}\) of the ionomer to improve the catalyst layer structure. In addition to these approaches, increasing the gas permeability\(^{[12,32]}\) is the most required for electrode ionomers. The following paragraphs provide a brief literature overview on the effects of different electrode ionomers on the performance.

The Role of the Ionomer Ion-Exchange Capacity: Similar to the ionomer content, there is also an optimal IEC to achieve the highest performance\(^{[31,58,90]}\). For example, Yoda et al.\(^{[90]}\) studied SPAES ionomer with two different IECs (1.8 and 2.5 meq g\(^{-1}\)) as electrode electrolyte (I/C = 0.7). At 60% relative humidity, they observed higher performance for the catalyst layer with the lower IEC (1.8 meq g\(^{-1}\)), while at 100% RH, similar performance was obtained for both IECs. The authors emphasize the importance of suppressing the adsorption of the ionomer on the Pt catalyst surface at low RH by using a low IEC (1.8 meq g\(^{-1}\)). On the other hand, a high IEC (>2.8 meq g\(^{-1}\)) enables high proton conductivity at low RH (<60% RH), as reported by Skalski et al.\(^{[31]}\). Furthermore, according to a recent study of Chowdhury et al.,\(^{[9]}\) higher IEC ionomers also feature an improved oxygen transport through the ionomer thin film due to greater water uptake and low crystallinity. Therefore, depending on the operation conditions, trade-offs between sufficient proton conductivity, oxygen transport, and interfacial resistance due to the adsorption of the ionomer on the catalyst surface must be carefully considered. Targets and challenges for ionomers in the catalyst layer are discussed in Section 3.2.

The Role of the Ionomer Molecular Weight: The ionomer molecular weight is another parameter, which potentially has a significant impact onto MEA performance, but was only scarcely studied in literature. Chae et al.\(^{[31]}\) recently investigated the effects of the molecular weight of SPAES (40% sulfonation degree) with three molecular weights: \(M_w = 12,000, 27,000,\) and \(51,000\) g mol\(^{-1}\) (polydispersity = 2) on the performance. They observed the highest peak power density with ~27 000 g mol\(^{-1}\), while the lowest overall performance was with 12 000 g mol\(^{-1}\). The authors suggested that the short polymer chains (of low molecular weight) lead to less connection between polymer aggregates. The result indicates that different ionomer molecular weights can lead to different porosities and interactions with the catalyst due to different entanglements of the polymer chains. However, as the molecular weight affects many of the abovementioned ionomer properties, it is very hard to study the effect separately without cross-effects.

The Role of the Ionomer Gas Permeability: As in recent work on PFSA-based MEAs, the design of novel, catalyst-layer-specific ionomers with higher gas permeability is key to boost high current density operation.\(^{[11,12,91]}\) Thus, for hydrocarbon ionomers with typically very low gas permeability, this is of even higher importance. Unfortunately, there have been only very few activities in literature addressing this. Yoon et al.\(^{[32]}\) replaced biphenyl groups in the polymer backbone of SPAES (IEC = 2 meq g\(^{-1}\)) with biphenyl fluorene group (fSPAES-70) to hinder chain packing of the bulky fluorene group in fSPAES-70. They observed an improved performance by 28% at 0.6 V under \(H_2/air\), 100% RH with no detrimental effects on durability.

Although the in situ experimental results are still early stage, the progress is tremendous compared to the early work on hydrocarbon ionomers, which are mainly ex situ and did not focus on hot/dry conditions. Improving the performance at high temperature and low humidification is more challenging for hydrocarbon ionomers, as the proton conductivity and the swelling behavior of hydrocarbons are much more sensitive to relative humidity compared to PFSA\(^{[19,92]}\) and the effects of hydrocarbon-based ionomer on the oxygen reduction reaction (ORR) kinetics are far less elucidated.

### 2.1.3. Performance at High Temperatures beyond >100 °C

Table 2 summarizes briefly the performance of fuel cells under operating temperatures beyond 100 °C reported in literature until 2021. Unfortunately, a comparison among the reported MEAs in literature is not possible due to different operation conditions, therefore, the two columns “power density at 0.7 V” and “peak power density” should rather serve as rough orientation than quantitative comparison. The performances of the fuel cells reported at these conditions drop significantly compared to those at 80 °C (compare Table 2). Remarkably, this drop in performance under hot and dry conditions is the least pronounced for short-side chain (SSC) PFSA.\(^{[93]}\) Challenges and possible perspectives for hydrocarbon-based fuel cells are discussed in Section 3.

### 2.2. Electrolyzers

#### 2.2.1. Electrochemical Performance

In PEM electrolysis, the reduction of gas crossover is of particular interest: first, the gas quality is impaired by parasitic gas crossover; second, at low current densities, an explosive \(H_2\) in \(O_2\) mixture can be formed on the anode side, if the \(H_2\) gas crossover is too high. This limits the lower operation regime of a water electrolyzer and makes countermeasures such as the use of additional Pt recombination catalysts necessary.\(^{[97]}\) In addition to low gas crossover, high mechanical strength is required due to operation under high differential pressures for the direct production of pressurized \(H_2\).\(^{[98]}\) To match those

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**Table 2**

| Temperature (°C) | Power Density (mW cm\(^{-2}\)) | Peak Power Density (mW cm\(^{-2}\)) |
|------------------|-------------------------------|----------------------------------|
| 80               | 300                           | 350                              |
| 100              | 250                           | 300                              |
| 120              | 200                           | 250                              |
| 140              | 150                           | 200                              |
| 160              | 100                           | 150                              |
requirements with PFSA ionomers, relatively thick membranes of about 50–180 µm are used, resulting in a high protonic resistance and thus, low voltage efficiency.[15] Therefore, hydrocarbon membranes – holding the promise of high protonic conductivity and low gas crossover – bare a huge potential for electrolysis applications.

However, literature on hydrocarbon MEAs used in water electrolyzers is still scarce and the reported performances were until recently often limited by poor catalyst utilization[99–103] or high interfacial PEM–CL resistances.[104] Figure 4 show an overview of current densities at 1.8 V of PEMWEs with different hydrocarbon membranes. Nolte et al.[99] and Linkous et al.[100] reported current densities of 30 mA cm$^{-2}$ at 1.8 V with SPAES and sulfonated poly(ether ketone) (SPEEK) as membrane, respectively. Jang et al.[101] fabricated MEAs with a polysulfone and poly(ether ketone) membrane, reporting a current density of 1 A cm$^{-2}$ at 1.8 V. With this, the group highly exceeded the previously reported voltage efficiencies of fluorine-free MEAs. However, the achieved current density is still lower than today’s state of the art. Albert et al.[102] fabricated MEAs with a radiation-grafted membrane based on combinations of styrene (St), acrylonitrile (AN), and 1,3-diisopropenylbenzene (DiPB) reaching 0.6 A cm$^{-2}$ at 1.8 V. While the reported voltage efficiency at low current densities was superior to a commercial PFSA MEA, the voltage efficiency at high current densities was limited by mass transport, most likely due to an unfavorable constitution of the electrodes. However, Wei et al.[104] found that not only an optimized electrode composition is of importance, but also a good electrode membrane interface is crucial to translate promising material properties of the reported polymer electrolytes into excellent voltage efficiencies. The authors fabricated MEAs using SPEEK as binder in the electrode and SPEEK blended with poly(ether sulfone) as membrane material. This fully hydrocarbon MEA reached a current density of 1 A cm$^{-2}$ at 1.8 V. When Nafion was used instead of SPEEK in the electrode as polymer binder, the voltage efficiency decreased drastically (0.15 A cm$^{-2}$ at 1.8 V). This was attributed to a high interfacial PEM–CL resistance caused by the use of different ionomers as binder in the electrode and PEM.

Other groups, however, achieved promising voltage efficiencies with hydrocarbon membranes and Nafion binder in the electrodes. Siracusano et al.[105] reached a current density of 1.1 A cm$^{-2}$ at 1.8 V with a sulfonated polysulfone membrane and Nafion containing electrodes. Smith et al.[106] achieved a respectable voltage efficiency with a microblock sulfonated poly(ether-ketone) membrane and Nafion binder (1.5 A cm$^{-2}$ at 1.8 V). Skulimowska et al.[107] presented a MEA with a sulfonated polybenzimidazole (sPBI) membrane and Nafion as electrode binder. Despite inhomogeneous deposited catalyst material due to dimensional changes of the sPBI membrane while spray coating the electrode material, a current density of 1.6 A cm$^{-2}$ at 1.8 V was achieved. Han et al.[38] reported high efficiencies of MEAs with biphenol-based sulfonated poly(arylene ether sulfone) membrane and Nafion electrode binder exceeding the Nafion NR212 reference (4.2 vs 3.7 A cm$^{-2}$ at 1.8 V).

Table 2. Literature overview of fuel cell performance under operating temperatures above 100 °C, operated in H$_2$/air conditions.

| Ref. | Operating conditions | Membrane material | Electrode electrolyte | Power density at 0.7 V [W cm$^{-2}$] | Peak power density [W cm$^{-2}$] |
|------|----------------------|-------------------|----------------------|--------------------------------------|----------------------------------|
| [94] | H$_2$/air, 120 °C, 30% RH, 101 kPa$_{abs}$ | Sulfonated poly(phenylene) containing tetrafluorophenylene, (SPP-QP-f) | Nafion D521 | 0.09 | 0.2 |
| [95] | H$_2$/air, 120 °C, 35% RH, 300 kPa$_{abs}$ | S360 PBOO blend | Nafion | 0.2 | 0.4 |
| [96] | H$_2$/air, 120 °C, 35% RH, 250 kPa$_{abs}$ | Sulfonated poly(arylene ether sulfone) (multiblock copolymer) | n/a | 0.2 | 0.3 |
| [89] | H$_2$/air, 120 °C, 40% RH, 150 kPa$_{abs}$ | SSC PFSA Aquion E87-05Sx | Aquion D78-20BS + PEC$^4$ | 0.1 | 0.2 |
| [59] | H$_2$/air, 110 °C, 50% RH, 250 kPa$_{abs}$ | Permion | Permion | 0.3 | 1.0 |
| [93] | H$_2$/air, 110 °C, 33% RH, 150 kPa$_{abs}$ | SSC PFSA Fumapem | 3 m SSC PFSA | 0.6 | 0.9 |
| | H$_2$/air, 110 °C, 33% RH$_{cathode}$ | SSC PFSA Aquion E79-03S | n/a | -0.1–0.2 | -0.4 |
| | | Nafion 111 | n/a | 0.1 | 0.2 |

$^4$Poly(ethylene glycol).
By varying the structure of polymers with similar IECs, Han et al.\textsuperscript{[38]} found hydrocarbon random copolymers superior to multiblock copolymers in respect to the ratio of voltage efficiency to gas crossover. This figure of merit not only provides a direction for future research but also shows the high advantage of hydrocarbon ionomers being able to be designed much easier than PFSA to adapt to specific requirements. These encouraging results reported by several groups confirm that combinations of PFSA and hydrocarbon materials are compatible if used in membrane and electrode and enable MEAs with state-of-the-art performance.

Only recently, fully hydrocarbon MEAs reached similar and superior performance to state-of-the-art PFSA MEAs. In our group, fully hydrocarbon MEAs based on sulfonated poly(phenylene sulfones) (sPPS) were shown to exhibit much higher voltage efficiencies compared to state-of-the-art Nafion N115 MEAs (3.5 vs 1.5 A cm\(^{-2}\) at 1.8 V).\textsuperscript{[107]} The improved performance was mainly attributed to a much lower ionic resistance of the sPPS membrane in comparison to the Nafion N115 with similar thickness. Also, Park et al.\textsuperscript{[108]} reported superior performance of fully hydrocarbon MEAs with a 20 µm sulfonated poly(arylene ether sulfone) membrane compared to MEAs with Nafion N115 membrane (2.2 vs 1.3 A cm\(^{-2}\)). The increased voltage efficiency of the SPAES MEAs was similarly attributed to the low Ohmic resistance of the thin SPAES membrane.

These recent findings clearly show the tremendous developments achieved within the past 2 years. In contrast to the current state of the art for fuel cells, where fully hydrocarbon MEAs meet PFSA benchmark performance only at high humidity, but still show a drop in performance when operated dry, the situation in electrolysis is different. As electrolyzer MEAs are typically operated in liquid water, at least on the anode side, state-of-the-art performance is met with both, fully hydrocarbon and hydrocarbon/PFSA-based MEAs. This is an encouraging result and should be the baseline for validation at full cell level or in the short stack.

**H\(_2\)** Crossover: Since the H\(_2\) crossover is critical for electrolyzers, measurement of the H\(_2\) permeation through the membrane is of particular interest. To meet the requirements of stability and reduce the H\(_2\) crossover, relatively thick PFSA membranes are employed in state-of-the-art electrolyzers.\textsuperscript{[97]} However, this leads to increased ionic resistance caused by the thick membrane. Reducing the membrane thickness reduces the resistance of the MEA but increases the H\(_2\) crossover following a 1-over-x trend according to Fick’s law of diffusion. H\(_2\) crossover measurements from Albert et al.\textsuperscript{[102]} illustrate this trend for Nafion membranes of different thicknesses (Figure 5). Thus, the use of membranes of one material class is always a trade-off between high crossover and high area resistance. As can be observed from Figure 5, new material classes like radiation-grafted hydrocarbon St/AN (purple triangles) and St/AN/DiPB (green squares) allow to reduce the H\(_2\) crossover while maintaining the same area resistance.\textsuperscript{[102]}

In line with the results from Albert et al.\textsuperscript{[102]} in our work,\textsuperscript{[107]} we also found a more than 3 times lower H\(_2\) crossover for sPPS-based membranes of similar thickness and much higher IEC compared to a Nafion N115 membrane despite a much lower area resistance of 57 ± 4 vs 161 ± 7 mΩ cm\(^2\). Similar to Albert et al.\textsuperscript{[102]} the H\(_2\) crossover in our work was measured in a fuel cell setup by linear sweep voltammetry while humidifying the membrane by water vapor. Increasing the relative humidity from 100% RH to oversaturated conditions yielded an almost threefold increase of the measured H\(_2\) crossover for the sPPS membrane due to increased water content in the membrane. While this change in conditions had a significant effect on the H\(_2\) crossover of the sPPS membrane, the H\(_2\) crossover of the N115 membrane only increased slightly due to the relatively lower water uptake compared to the sPPS membrane. However, despite the higher increase in H\(_2\) crossover of the sPPS membrane, the measured H\(_2\) crossover current density remained well below the value of the N115 membrane, especially taking into account the much higher proton conductivity of the sPPS membrane.

Han et al.\textsuperscript{[38]} also reported a more than 3 times lower H\(_2\) permeability of the random and multiblock BPSH membranes compared to an only 50 µm thin Nafion NR212 membrane. While both, random and multiblock BPSH membranes show reduced H\(_2\) crossover, the random BPSH membranes further decrease H\(_2\) permeation due to narrower and less connected domains. While the H\(_2\) permeation is affected by the change in morphology between random and multiblock membranes, the proton conductivity is almost similar. Thus, the random BPSH membrane has a slightly better figure of merit given as ratio of proton conductivity to H\(_2\) permeation.

These findings show the high potential hydrocarbon membranes have in electrolysis. However, it also points out the necessity to adjust the conditions for the H\(_2\) crossover to the conditions present in a real electrolyzer system and ideally align it with in situ measurements during electrochemical characterization.

### 2.2.2. Degradation in Electrolysis Operation

Since membranes in electrolysis are constantly humidified by liquid water, changes in relative humidity are not as relevant...
as in fuel cells. However, inhomogeneity in water distribution caused by insufficient gas removal still can lead to local dry out and with this, mechanical stresses due to uneven membrane swelling.\cite{109,110} Additionally, assembly in the cell stack and operation under high differential pressures can cause mechanical stress and with that can lead to failure of the system.\cite{109,110}

The mechanical stresses are even more problematic for hydrocarbon materials with their high water uptake in liquid water, which can lead to softening and mechanical instability.\cite{38,107}

Chemical degradation of hydrocarbon membranes may be stronger in electrolysis compared to fuel cells due to the higher gas crossover via fully developed hydrophilic aqueous domains and with that, accelerated radical formation. However, to which extent chemical degradation contributes to the low lifetimes reported in literature is not clear yet and needs to be further investigated. The few studies reporting continuous operation in standard conditions of hydrocarbon MEAs showed lower stability than PFSA MEAs.\cite{38,107} The observed degradation was hypothesized to be caused by softening of the membrane and chemical degradation. Additional to degradation of the membrane, Han et al.\cite{38} attributed the reported higher degradation rates of the hydrocarbon MEAs compared to the PFSA MEAs to delamination of the electrodes, which contained Nafion as ionomer binder. However, it becomes obvious that studies investigating the long-term stability and degradation mechanism of hydrocarbon MEAs in electrolysis are scarce but urgently required in order to target the polymer design not only toward high voltage efficiencies and low gas crossover but also toward mechanical and chemical stability.

2.2.3. Electrode Ionomer Content

To the extent of the authors' knowledge, only three studies exist where hydrocarbon materials were utilized as ionomer binder in electrolysis electrodes.\cite{104,107,108} Wei et al.\cite{104} fabricated electrodes using 15 wt% SPEEK as electrode binder, showing a lower voltage efficiency than a reference with the same weight concentration of Nafion as ionomer binder. In recent work from our group, we used sPPS with an IEC of 2.78 meq g$^{-1}$ as ionomer binder (for more details, see Schuster et al.\cite{29}). With 4 wt% sPPS ionomer in a conventional iridium oxide catalyst layer and 10 wt% ionomer content in a conventional Pt/C cathode catalyst layer, superior voltage efficiency and similar kinetics were reported compared to the PFSA reference with higher ionomer binder weight concentrations (anode: 8 wt%, cathode: 28 wt%). The comparably low sPPS ionomer contents used in this test are linked to the high swelling properties of the used sPPS in liquid water ($\lambda_{sPPS} = 28$). With SPAE as ionomer binder, Park et al.\cite{108} also found an optimized voltage efficiency for ionomer contents of 5 and 10 wt% in the anode and cathode electrodes, respectively. The utilized SPAE had an IEC of 2.78 meq g$^{-1}$ and a similar water uptake ($\lambda_{SPAE} = 27$) as the sPPS.

Thus, from the small amount of published data on hydrocarbon catalyst layer data, only first trends can be derived to facilitate future catalyst development. For the rate-limiting anode side, typically low contents of 4–5 wt% ionomer in solids seem to yield optimized performance, especially when ionomers with high water uptake are used. To date, studies on ionomer content in respect to the swelling characteristic of the ionomer are missing. The cathode side typically matches the composition of fuel cell cathodes in terms of Pt loading and ionomer content. However, the stronger swelling of hydrocarbon materials in liquid water and with that, insufficient gas removal due to pore blocking needs to be considered and might lead to lower optimum ionomer contents in electrolysis compared to fuel cells. However, the cathode side is not performance-limiting and thus maybe not in the main focus of parameter optimization.

Some studies combined electrodes with PFSA ionomer binders and hydrocarbon membranes. Wei et al.\cite{104} combined Nafion electrodes with a SPEEK/PES membrane and reported much lower performance than a fully hydrocarbon MEA. In contrast to that, Han et al.\cite{38} did not report hindered performance when using PFSA as ionomer binder and a hydrocarbon membrane; they reported delamination issues with no catalyst layer remaining on the hydrocarbon membrane after 90 h of stress test. Both studies emphasize the importance of a good interfacial compatibility between membrane and ionomer binder in the electrode, if different ionomer chemistries are used.

As important as electrode adhesion is the deposition process of the electrode. Due to strong swelling of the hydrocarbon membranes, direct deposition of the electrodes onto the membrane, e.g., by casting or spray coating might hinder uniform electrode deposition and with that, leading to kinetic losses.\cite{103} Prior deposition onto a sheet and subsequent transfer onto the membrane was also reported.\cite{38,104} This method circumvents the swelling issue, however, high glass transition temperature characteristic for hydrocarbon materials can impede a good transfer by the decal method. Only hydrocarbon polymers with high intermolecular force allow decal transfer near the $T_g$ of the polymer.\cite{104}

To summarize, both PFSA's and hydrocarbon-based ionomers can be applied as membrane and electrode electrolyte in fuel cells and electrolyzers. Each of them has the advantages and disadvantages for their applications, which are summarized in Table 3.

Knowing the advantages and disadvantages of each material, the following section will address the challenges and perspectives for next-generation hydrocarbon-based MEAs.

3. Challenges and Perspectives for Next-Generation MEAs

Membrane and catalyst layer ionomers have different requirements. For instance, while the ionomer for the membrane needs to possess a low gas permeability for a low gas crossover, the ionomer binder for the catalyst layer should have a high gas permeability to reduce transport resistance. The following sections separate the challenges and perspectives for membranes and electrodes to emphasize the need to develop separate ionomers for individual application.

3.1. Proton Exchange Membranes

There have been drastic improvements made in the electrochemical properties of hydrocarbon membranes in terms of
proton conductivity and durability. However, two weak points of this material class remain. First, the improvement of proton conductivity at low RH is a crucial parameter for future applications, which requires further optimization on ionomer level. Second, on experimental cell level, promising mechanical and chemical fuel cell durability (>1000 h open circuit voltage (OCV) and >30 000 RH cycles)\textsuperscript{[9]} was demonstrated, but not proven on full size cell yet or short stack level. In the following sections, challenges and possible future directions for membranes in fuel cells and electrolyzers are discussed.

3.1.1. Proton Conductivity

A common requirement for both electrolyzers and fuel cells is the high proton conductivity. For PFSAs, often, “the same” ionomer is employed for electrolysis and fuel cells and the fundamentally different operation conditions are accounted simply by adjusting properties like membrane thickness and/or a membrane reinforcement. For example, typically 50–150 µm membrane thicknesses are used in electrolyzers due to higher differential pressures, and expanded-PTFE (ePTFE)-reinforced membranes of around 15 µm thickness to achieve the lowest possible protonic resistances are employed in fuel cells. Due to the intrinsic high mechanical strength of several hydrocarbon materials, thinner hydrocarbon membranes could be used for both applications. Alternatively, the thickness could be similar to the state of the art for lower gas crossover and higher durability without compromising performance due to the higher protonic conductivity at high humidity (>80% RH) in most hydrocarbon materials.

The strong dependence of hydrocarbon membranes’ proton conductivity on water content is not critical for electrolyzers since they are operated in liquid water yielding fully developed hydrophilic aqueous domains with good connectivity. In contrast to that, fuel cell membranes should have a high proton conductivity over a wide range of temperature and humidity for cold/wet (e.g., 50 °C, 90% RH) and hot/dry (e.g., >80 °C, 30% RH) conditions. Knowing these distinct requirements, different membrane (ionomer) development strategies should be considered for each system.

Figure 6 summarizes proton conductivity data from materials developed in the groups of Long and Miyatake\textsuperscript{[94]} and Holdcroft and co-workers,\textsuperscript{[33,111]} which enabled also promising performance in fuel cells at 80 °C and varying humidities. Nafion 211 (taken from ref.\textsuperscript{[33]} and low equivalent weight (EW) (<800) PFSA (taken from ref.\textsuperscript{[112]}) are provided as benchmark. The proton conductivities of state-of-the-art fluorine-free ionomers (sPPP-1 RCP, sPPB-db2, and sPP-QP-3.1, Figure 6) are comparable to state-of-the-art PFSAs at high humidity (>80% RH). However, the values at low humidity (<40% RH) are still apart from the target for proton conductivity for automotive application (=0.1 S cm\textsuperscript{-1})\textsuperscript{[113]} as well as slightly below the typically reported values for state-of-the-art short-side chain PFSA ionomers.\textsuperscript{[3]} Only the partially fluorinated hydrocarbon ionomer (sPP-QP-f-4.1, Figure 6) enabled higher proton conductivity than low EW PFSA even at 40% RH.\textsuperscript{[94,114,115]}

As the requirements for RH dependence and proton conductivity diverge for electrolysis and fuel cells, a separate optimization might be required, which is a particular advantage of hydrocarbon materials. For instance, the “window of properties” is significantly wider compared to PFSAs: ion exchange
capacities range between 1 and 4 meq g\(^{-1}\) in contrast to PFSA (1–1.3 meq g\(^{-1}\))\(^{[8,116]}\). Increasing the IEC of a hydrocarbon-based ionomer typically increases its proton conductivity in both low and high humidity (sPPB-0.5 RCP vs sPPP-1 RCP, Figure 6), while for PFSA-based ionomers, the difference in high humidity is less pronounced as in low humidity (Figure 6). As a result, high IEC ionomers would be preferred in fuel cells due to the higher proton conductivity in lower humidity.

The barrier for proton conduction in ionomers like PFSAs or hydrocarbon-based ionomers can be estimated in form of activation energies. As activation energies typically decrease with increasing humidity\(^{[117]}\) and change with structural characteristic of an ionomer, the proton conductivity increases with higher degree of sulfonation\(^{[24]}\) higher acidity\(^{[118,119]}\) and/or a more pronounced hydrophilic/hydrophobic phase separation\(^{[117]}\). Therefore, the activation energy may be used as an intrinsic characteristic in order to compare different novel hydrocarbon ionomers to state-of-the-art materials.

In the liquid environment of an electrolyzer, the difference is smaller than in fuel cell operation with fluctuating humidity. In addition, at high humidity or in liquid water, high IECs (\(\geq 3\) meq g\(^{-1}\)) cause strong swelling, which deteriorates the mechanical stability of the membrane.

An approach to decrease water uptake and dimensional swelling is molecular branching of the ionomer\(^{[111]}\). The proton conductivity of a branched sPPB (sPPB-db2) was greater than its linear, unbranched analog (sPPB-d0 vs sPPB-db2, Figure 6). Under low humidity (<60%), the improvement was greater than under high humidity. The result confirmed that pronounced phase separation is a promising direction toward improved proton conductivity at low humidity.

Adding fluorinated moieties or other hydrophobic components (e.g., bis-tetracyclone\(^{[13]}\), quinquephenylene\(^{[120]}\)) into the backbone of the ionomer can enhance phase separation, and hence, significantly improved proton conductivity in lower RH \(^{[94,96,114]}\). Although these polymers may not be fluorine-free, these studies emphasize the importance of a phase-separated morphology. It is believed that controlling the sequence of the hydrophilic/hydrophobic components\(^{[120]}\) (at the same IEC) and water retention\(^{[96]}\) relating to hydrophilic domain size in membranes can improve the proton conductivity under low humidity and intermediate temperature conditions.

As mentioned in Section 2.2, Han et al.\(^{[18]}\) reported only minor disadvantages in proton conductivity for random polymers in contrast to multiblock polymers but major advances in gas crossover. Hence, more tortuous hydrophilic domains of random polymers may be more advantageous for water electrolyzer membranes than multiblock polymers as they may maintain good proton conductivity while decreasing gas permeation.\(^{[18]}\) Thus, although multiblock polymers show advantageous properties over random polymers in fuel cells – due to their enhanced phase separation – there might be a different optimum under immersed conditions for electrolysis.\(^{[18]}\)

### 3.1.3. Chemical Stability

To improve the chemical stability of membrane ionomers, it is important to understand the radical attack and chemical degradation mechanism of hydrocarbon-based membranes (for detailed studies, see Holmes et al.\(^{[26]}\) or Gubler et al.\(^{[124,137]}\)).
Two common approaches to improve the chemical stability of membranes are doping the membrane with 1) phenolic compounds, e.g., pyridine or 2) cerium ions (Ce³⁺) and oxides thereof. Cerium is still considered the most effective radical scavenger known in PFSA-based fuel cells, thanks to the ability to regenerate by redox cycling between Ce⁴⁺ and Ce³⁺ in the presence of H₂O₂. Despite the lower scavenging rate of Ce³⁺ (10⁸ m⁻³ s⁻¹) compared to the attack rate of radicals on the aromatic compounds (10⁴–10¹⁰ m⁻³ s⁻¹) [all values determined in aqueous solutions and ambient temperature], some studies observed positive effects of cerium-based additives on the chemical stability of the hydrocarbon-based membrane. For instance, Lee et al. reported that their composite-hydrocarbon-based membrane with 2 wt% cerium nitrate hexahydrate achieved over 2200 h under in situ accelerated OCV durability testing following the U.S. DOE protocol, while the reference membrane achieved less than 700 h, which is still higher than the 2025 target (500 h). However, to meet the target of the fuel cell system lifetime for heavy duty vehicles, other antioxidants might be required that also feature the ability of regeneration, but have a higher reaction rate constant with OH⁻ radicals than that of aromatic compounds.

3.1.4. Alternative Approaches

In order to meet the manifold demands for proton exchange membranes in fuel cells and other electrochemical applications, efforts are also taken beyond classical polymeric electrolytes. The high freedom in molecular design of hydrocarbon-based building blocks allows the design of tailored nanoporous organic materials with promising properties. Examples were demonstrated as hyper-cross-linked polymers, conjugated microporous polymers, covalent organic framework, and polymers of intrinsic microporosity. These tailored materials go beyond established design of polymer chains and could set new benchmarks in future. Furthermore, inorganic polyoxometalates (POMs) in a polymer matrix showed encouraging effects. Due to the high acidity, good thermal stability and chemical adjustability of POM, high proton conductivities in hot/dry conditions were demonstrated. However, the homogeneous distribution and immobilization of POM in the polymer matrix remain challenging.

3.2. Hydrocarbon Ionomers in Catalyst Layers

3.2.1. Processing of Catalyst Inks

For each hydrocarbon-based ionomer, specific catalyst ink formulations and properties (e.g., viscosity, wetting properties, surface tension, etc.) are required depending on the deposition method. For instance, sulfonated polyphenylenes can be dispersed in conventional alcohol/water inks, which facilitates the fabrication of MEAs with parameters comparable to PFSA-based MEAs. Other materials, such as sulfonated polyphenylene sulfones, however, require high boiling point solvents. On laboratory-scale fabrication, ultrasonic spray coating is established as method of choice for rapid prototyping of MEAs requiring only a small amount of catalyst (<100 mg). However, the feasibility and the reproducibility of catalyst ink mixing and depositing procedure can differ significantly between lab scale and mass production. The transition from spray coating to scalable coating methods was not reported yet in literature, but is a critical step toward commercialization of this technology.

In addition, the typically employed decal-transfer process to laminate catalyst layers onto the membrane is challenging due to very high glass transition temperatures of most hydrocarbon materials. Therefore, direct coating of the catalyst layer onto a membrane might be the preferential fabrication route. This has significant impact onto mass production of hydrocarbon MEAs, since decal transfer on roll-to-roll coating machines is the current state of the art. Direct coating of the membrane, which is also a goal of PFSA-based MEAs to reduce cost, might put additional requirements to the properties of the hydrocarbon membrane, namely limited swelling in the ink solvents. Again, membrane reinforcements could also alleviate this challenge.

Towards the Performance of PFSA Electrodes – The Challenges of Hydrocarbon Electrodes: Even with optimized ionomer content, ion exchange capacity, and solvent systems, hydrocarbon MEAs feature inferior performance compared to state-of-the-art PFSA MEAs even at high humidity (>80% RH) and especially in the kinetic region (E > 0.7 V). The inferior performance of hydrocarbon MEAs at high humidity and at high cell potentials might be linked to 1) a lower ECSA, 2) a lower oxygen permeability of hydrocarbon ionomers, and 3) a slightly lower proton conductivity of hydrocarbon ionomers in the catalyst layer. The reported ECSAs of catalyst layers with Pt and hydrocarbon-based ionomers (between 40 and 60 m² g⁻¹) were observed to range about 30–40% below that of PFSA counterparts (between 70 and 90 m² g⁻¹, at a Pt loading of 0.4 mg cm⁻²). As mentioned in Section 2.1, while PFSA molecules form a rod-like or colloidal dispersion, it is believed that hydrocarbon ionomers exist in solution as weakly bound aggregates and can penetrate the primary pores of the carbon particles and block the Pt surface. However, there is still no clear evidence for such interactions to date. Another presumption that has not yet been experimentally verified is the catalyst poisoning via anion adsorption due to the higher IEC or to phenyl poisoning. These phenomena could also lead to a lower ECSA or to a lower exchange current density of hydrocarbon-based CLs, which may influence the ORR kinetics. It is observed that the exchange current density of Pt/C with hydrocarbons is typically lower than with PFSA, indicating that the oxygen reduction reaction rate is higher with PFSA than with hydrocarbon ionomers, e.g., SPEEK. For instance, the exchange current densities of MEAs with SPEEK ionomer (~10⁻¹¹ A cm⁻²) is reported by Astill et al. to be an order of magnitude lower than that with Nafion (~10⁻³–10⁻⁵ A cm⁻²) under 30–50 °C, 100% RH, and 200 kPa. The lower exchange current density of Pt/C with hydrocarbon ionomers could be attributed to the lower oxygen permeability compared to PFSA, Sambandam et al. experimentally determined the oxygen transport resistance (through an ionomer film) via limiting current. The oxygen transport resistances of SPEEK (2.2 s cm⁻¹) and of sulfonated polysulfone (SPSU) (3.0 s cm⁻¹) were reported to be higher than that of Nafion (1.6 s cm⁻¹).
The Tafel slopes of hydrocarbon-based MEAs with Pt and hydrocarbon-based ionomers are typically 10–20 mV dec\(^{-1}\) higher than those of PFSA MEAs\(^{[154,155]}\). The higher Tafel slopes could be related to a suboptimal electrode kinetics, but it is often misinterpreted, as mass transport losses in the electrolyte phase could also increase the Tafel slope\(^{[158,159]}\).

It was shown in several studies with PFSA-based cells that the kinetic performance of fuel cells can be improved by replacing Pt with more active catalyst materials, e.g., Pt alloys\(^{[160]}\). In our group, we reported that the Tafel slope of the polyphenylene-based cells with PtCo/C (74 mV dec\(^{-1}\)) was comparable to that of the PFSA-based cells (73 mV dec\(^{-1}\)) with the same catalyst and under the same operating condition (H\(_2\)/O\(_2\), 95% RH).\(^{[59]}\) The ECSAs of both cells were similar, indicating a reduction in kinetic losses when PtCo substitutes Pt. However, the reported mass activity at 900 mV corrected for high frequency resistance (900 mV\(_{\text{HFR-free}}\)) of the PtCo/hydrocarbon-based cells (56 mA mg\(_{\text{Pt}}\)) is still lower than that of their PFSA counterparts (74 mA mg\(_{\text{Pt}}\))\(^{[59]}\).

It was shown in many studies that the proton resistances of hydrocarbon-based catalyst layers are slightly lower than that of PFSA-based layers, even at high humidity. For instance, the proton resistance of a catalyst layer with 15 wt% sPPB (0.63 \(\Omega\) cm\(^2\)) is 2 times the resistance of a reference with 30 wt% Nafion (0.32 \(\Omega\) cm\(^2\)) under fully humidified gas feeds despite the higher IEC (3.19 meq g\(^{-1}\)) of the sPPB–H\(^+\) ionomer.\(^{[17]}\) The higher protonic resistance of the sPPB–H\(^+\) catalyst layer is presumably linked to the lower ionomer content in the hydrocarbon catalyst layer that likely results to a poor connected ionic network\(^{[8,17]}\) or possibly due to a less pronounced hydrophilic/hydrophobic phase separation in the catalyst layer.\(^{[165]}\)

At low humidity (<50% RH), the relative magnitude of individual contributions to the performance losses of hydrocarbon-based MEAs is far less elucidated than that of PFSA-based MEAs and requires further investigation. For PFSA-based MEAs, the magnitude of the contributions to the potential losses was intensively studied. For example, Neyerlin et al.\(^{[162]}\) and Liu et al.\(^{[68]}\) investigated how the humidity affects the catalyst layer proton resistance. Neyerlin et al.\(^{[162]}\) reported a threefold higher cathode resistance at 60% RH than at that at 10% RH at lower current densities (<300 mA cm\(^{-2}\)), leading to a two-fold decrease in the ORR exchange current density due to the reduced proton activity. Liu et al.\(^{[68]}\) showed that the cathode proton resistivity increased from \(\approx 20 \Omega\) cm at 122% RH (DE2021 ionomer, DuPont, I/C = 0.8) to \(\approx 200 \Omega\) cm at 50% RH with the same cathode ionomer and at the given I/C ratio. As a result of reduced humidity, the connectivity of the ionomer network in the catalyst layer is certainly affected, leading to a reduction in catalyst utilization.\(^{[81]}\) The change in active areas can be partially seen in cyclic voltammograms.\(^{[59,161,164]}\)

The oxygen permeability of a Nafion thin film is observed to decrease with decreasing humidity. For example, Novitski and Holdcroft\(^{[165]}\) observed a decrease in oxygen permeability at 70 °C by a factor of 1.7 for a Nafion 211 membrane and of 3.4 for films drop-casted from Nafion DE2021 ionomer solutions on the Pt microelectrode (drying under ambient conditions), when the humidity is reduced from 90% to 30% RH. Kudo et al.\(^{[166]}\) also observed a decrease in oxygen permeability of a casted Nafion thick film (DE2020, 100 μm) by a factor of \(\approx 2\) when the humidity is reduced from 90% to 30% RH, both at 80 °C.

Future work should be dedicated to separate, and ideally, to determine the ratio of each individual contribution to the potential losses, especially at low current densities and low humidity to identify the key for the design of novel hydrocarbon-based MEAs. We believe that the general issue of hydrocarbon-based ionomers is the low gas permeability,\(^{[166]}\) which could be even more critical at lower humidity as for the case of PFSA\(_{\text{S}}\).\(^{[165]}\) At dry conditions (<30% RH), the main issue is the absence of water, which leads to a low proton conductivity of not only the membrane but also the electrode that results in a lower catalyst utilization.\(^{[59,81]}\)

Whereas the hydrogen oxidation reaction (HOR) is highly reversible in fuel cells, the oxygen evolution reaction (OER) is the limiting half-cell reaction in electrolyzers. To date, OER kinetic parameters are determined by ex situ experiments, e.g., rotating disk electrode,\(^{[167]}\) which may not be translated into in situ performance, as for the case of fuel cells.\(^{[168]}\) The discrepancy between ex situ and in situ performances is hypothesized to be due to other properties of the catalyst layers, e.g., ionomer distribution, mass transport resistances, etc.\(^{[168]}\) which have great impacts on the MEA overall performance.

While the kinetic parameters of the ORR on Pt in fuel cells was determined 15 years ago via in situ experiments,\(^{[159]}\) those of the OER on IrO\(_2\) was recently determined by Schuler et al.\(^{[167]}\) via “vapor-fed polymer electrolyte water electrolysis” by the combined variation of catalyst loading and temperature. The discrepancy in understanding the OER on IrO\(_2\) and the ORR on Pt is mainly due to the limitation of appropriate methodologies for characterization of electrolyzers,\(^{[167]}\) especially for in situ experiments. Bernt and Gasteiger\(^{[169]}\) proposed to extract the Tafel slope of OER catalysts in the current density region similar to fuel cells (10–100 mA cm\(^{-2}\))\(^{[92,159]}\) and to quantify the mass activity of OER catalysts at 1.45 V\(_{\text{iR-free}}\) in analogy to the quantification of the mass activity of ORR catalysts in fuel cells at 0.9 V\(_{\text{iR-free}}\)\(^{[160,170]}\). However, kinetic parameters (e.g., exchange current density \(i_{\text{a,c}}\), activation energy \(E_a\), and the reaction order \(\gamma\) of OER on IrO\(_2\) cannot be extracted as precisely as of HOR or ORR on Pt in fuel cells\(^{[159]}\) via Tafel analysis of in situ experiments, as it is difficult to determine the ECSA of IrO\(_2\) during in situ experiments. Iridium oxide catalysts does not feature the characteristic hydrogen underpotential deposition (H\(_{\text{upd}}\)) fingerprint, in contrast to Pt-based catalysts.\(^{[167,171]}\) Nevertheless, the ECSA of IrO\(_2\) can be accessed either via mercury underdeposition potential\(^{[172]}\) or zinc adsorption.\(^{[173]}\)

Reports on hydrocarbon ionomers utilized as binder in electrolysis electrodes are scarcer than in fuel cells, and research on the effects of hydrocarbon ionomers on the ECSA and catalytic activity is still missing to compare with PFSA\(_{\text{s}}\). However, Klose et al.\(^{[167]}\) reported similar iR-free voltages when hydrocarbons or PFSA were used as ionomer binder. This might be attributed to a high water uptake of the utilized sPPB ionomer in liquid water, which implies an increase of the gas permeability and the proton conductivity through the ionomer binder. As for fuel cells, improved performances were found with lower gravimetric ionomer contents when hydrocarbon ionomers are used as ionomer binder instead of PFSA\(_{\text{s}}\).\(^{[167,170]}\) Due to increased swelling when exposed to liquid water, an even lower hydrocarbon ionomer content as for fuel cells might be suitable to use in electrolyzer electrodes.
Based on these understandings, we emphasize not only the need to improve further understanding on interactions in the catalyst layer, but also the need to develop a novel ionomer for the catalyst layers. The novel ionomer should have higher gas permeability and decent proton conductivity at low humidity but simultaneously should not have a too high interfacial resistance to the catalyst, which can be accounted to, for instance, the high anion concentration. Requirements and targets for fuel cells and electrolyzers are discussed in the following sections.

3.2.2. Novel Distinct Hydrocarbon-Based Ionomers for the Catalyst Layer

To date, ionomers developed for membranes are applied in the catalyst layer. Most likely, the common assumption that high-performing membrane ionomer will also perform sufficiently as ionomer binder in the electrode (as was the case for Nafion) has led most research groups to focus solely on the development of novel membranes. As a result, the development and understanding of hydrocarbon ionomers as catalyst binders was not of particular importance so far.

Considering the different requirements for catalyst layer ionomer and membrane ionomer, it is quite clear that the use of identical ionomer for both layers might not be the best choice. In the catalyst layer, the highest gas diffusion rates, low interaction with Pt surfaces, decent proton conductivity, chemical stability, and reduced swelling are desired. This largely diverges from the properties required in the membrane, where low gas permeation, high conductivity, very low swelling, mechanical and chemical durability are required. In particular, the development of highly oxygen permeable hydrocarbon ionomers for the catalyst layers has not been considered by now but will most likely enable strong improvement of the performance of fully hydrocarbon MEAs, especially for fuel cells.

To achieve high performance fuel cell MEAs with hydrocarbon-based ionomer in the catalyst layer, the ionomers should

1) be miscible with the membrane ionomer, i.e., possess a good adhesion with the membrane and a similar swelling behavior,
2) enable well-connected hydrophilic domains to guarantee the high proton conductivity (≈0.1 S cm\(^{-1}\) at <60% RH),
3) reduce swelling at high RH (≤200% H\(_2\)O uptake in boiling water),
4) feature a low affinity for detrimental anion adsorption onto the Pt catalyst surface,
5) withstand elevated operation temperatures (100–120 °C),
6) enable high oxygen permeability to reduce the oxygen resistance (through ionomer thin film and Pt/ionomer interface).

For electrolysis, these requirements are different due to the liquid water environment and the iridium oxide catalyst.

As the permeability of molecules through polymers is the product of diffusivity and solubility within the ionomer, improving oxygen diffusion and solubility of the electrode ionomer is critical. The oxygen diffusivity of state-of-the-art highly oxygen-permeable ionomer (HOPI) is \(\approx 3 \times 10^{-10}\) m\(^2\) s\(^{-1}\) at 30% RH and \(\approx 5 \times 10^{-10}\) m\(^2\) s\(^{-1}\) at 90% RH, both at 80 °C.[12] As a rough comparison, the oxygen diffusivity of SPEEK (1.4 \times 10^{-10} m^2 s^-1) and that of SPSU (0.3 \times 10^{-10} m^2 s^-1) was observed to be lower than that of the Nafion reference (6.2 \times 10^{-10} m^2 s^-1) at the same conditions (80 °C, 75% RH, and 166 kPaab).[156]

While the reported oxygen diffusivities at 80 °C are in the same order of magnitude (\(\approx 10^{-10}\) m\(^2\) s\(^{-1}\)), the high oxygen solubility of HOPI (\(\approx 10\) µmol cm\(^{-3}\) atm\(^{-1}\) at 30% RH and \(\approx 7\) µmol cm\(^{-3}\) atm\(^{-1}\) at 90% RH, both at 80 °C) was reported to be the key for the improved power density.[12] As a rough comparison, the oxygen solubility of SPEEK (0.3 µmol cm\(^{-3}\) under 75% RH, 80 °C, and 166 kPaab) and SPSU (0.2 µmol cm\(^{-3}\) under 75% RH, 80 °C, and 166 kPaab) were observed to be more than an order of magnitude lower than the reported values for HOPI.[12] The results of the studies quantitatively confirmed that it is essential to synthesize highly oxygen-permeable nonfluorinated hydrocarbon-based ionomer for the catalyst layers to minimize the oxygen transport resistance.

Given the different desired properties for fuel cells and electrolyzers, it is critical to synthesize distinct fluorine-free hydrocarbon-based ionomers with suitable chemical structures, IEC, and MW for high performance electrodes and long-term stability under the hot/dry conditions (fuel cells) or in liquid water (electrolyzers). Various sophisticated characterization methods were established for PFSA-based fuel cells in the past years, which will significantly advance the understanding of hydrocarbon MEAs. For instance, oxygen limiting current[175] or hydrogen limiting current experiments[176,177] can be used to estimate the dry and wet oxygen diffusion resistances in the catalyst layer. Capacitance coverage determination[175] and dry proton accessibility measurements (i.e., measuring ECSA of the catalyst as a function of relative humidity using CO oxidation in MEA)[178,179] may give information on ionomer coverage and distribution in the catalyst layer, in-depth study of cyclic voltammetry data or H\(_2\)/N\(_2\) impedance spectroscopy[168] can reveal catalyst utilization or ionic resistances in the catalyst layers.

As detrimental properties in the catalyst layer such as low gas permeability and high anion group adsorption might be even expressed stronger with hydrocarbon ionomers than in PFSA-based MEAs, developing a dedicated hydrocarbon ionomer for the catalyst layer might have a strong lever on catalyst activity and mass transport properties. Furthermore, performance-limiting properties such as the ionomer–catalyst and ionomer–carbon interaction should be included in the development.[67,68,147,179]

3.2.3. Tailoring the Catalyst Layer

Besides engineering the pore volume in the catalyst layers with additives such as porogens or wetting agents, several approaches have been shown to be effective for tailoring the ionomer distribution in the catalyst layer, e.g., with chemically modified carbon supports.[74,184] Ideally, the ionomer should be distributed homogeneously in the catalyst layer for a highest possible ECSA, a lowest oxygen transport resistance, and a sufficient proton conductivity. However, the ionomer distributes randomly in the catalyst layer, leading to inhomogeneous
coverage on catalyst particles. By introducing N-functional groups on the carbon supports, which should interact with the ionomer chains, the distribution of ionomer can become more homogeneous.\cite{74,84} The studies showed to have positive effects on fuel cell performance, especially under dry operating conditions.\cite{74} To date, these approaches have not been adapted for hydrocarbon-based catalyst layers, but these could be promising approaches to improve the performance of hydrocarbon-based fuel cells in dry operating conditions.

3.2.4. Conditioning

For PFSA-based fuel cells, it was shown that significant gain in performance could be achieved by the introduction of a voltage recovery procedure at low cell voltages,\cite{186} low temperature, and high humidity, removing the undesired species such as sulfate groups on the catalyst. Since hydrocarbon materials feature completely different solvents, ionomer distribution, and ionomer/catalyst interaction in the catalyst layer, different conditionings might be required to further increase the performance. For both systems, electrolysis and fuel cell, the conditioning procedure is a nearly untouched field and should be included in future fully hydrocarbon MEA development.

3.2.5. Measurement Methods

To allow better comparison among data reported in literature, especially in the context of water electrolyzers, a uniform measurement method to examine the gas crossover is required. Since the humidity highly influences the gas crossover,\cite{181} we propose to determine the H₂ in O₂ content in situ and align it with in situ electrochemical characterization.

4. Conclusions

The rapid development of novel hydrocarbon ionomers enables now for the first time to build fully hydrocarbon MEAs that approach the performance of state-of-the-art PFSA-based MEAs in fuel cells and electrolyzers. However, there remain several hurdles for fully fluorine-free MEAs toward commercializable electrochemical applications. Specific ionomers for the catalyst layers, thorough proof of durability at scale, and an increase in understanding of catalyst–ionomer interactions and degradation phenomena can pave the way to the commercialization of fluorine-free MEAs. Based on the findings summarized in this perspective article, we emphasize the importance of intensifying the R&D activities on fully hydrocarbon MEAs. Given the very promising materials recently developed by polymer chemists worldwide, being available now in reasonable quantities and batch-to-batch consistency, the next important step is to focus on MEA engineering aspects to enable a fast “material-to-MEA” transfer. Facing the global\cite{193} and European\cite{181} mid-term goals to avoid fluorinated materials, and typical times for development cycles in automotive or chemical industry, an acceleration of fully hydrocarbon MEA development is required now to enable a successful commercialization of hydrocarbon ionomers and membranes in fuel cells and electrolyzers before 2030.

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Conflict of Interest

The authors declare no conflict of interest.

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