State of the Art Comparison Between Polymer Electrolyte Membranes for Hydrogen Fuel Cell Applications

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Abstract

Proton-exchange membrane fuel cells (PEMFCs) have been appealing for all sorts of applications and have been in use for many years, mainly for transportation applications because of new developments that have increased efficiency and power density while lowering operating temperature. However, in order to increase commercial viability and broaden use cases, PEMFCs must become more efficient. New research and developments in different polymer electrolyte membranes (PEMs) such as perfluorosulfonic acid membranes (PFSAs) and polybenzimidazole membranes (PBIs) have sought to increase efficiency and power density. This literature review focuses on state of the art proton membrane technologies such as PFSA, hydrocarbon-based, and PBI membranes. It provides a comprehensive review of basic fuel cell chemistry, mechanisms of function for these membranes as well as advantages and disadvantages, developments in the past few years, and an outlook as to where PEMFC technology will bring us in the future. PFSA membranes are the most widely used membrane currently, with Nafion™ currently dominating the market for PEMs. They have a high enough conductivity to be commercially viable, and have been in the market for decades. Hydrocarbon-based membranes are on the rise because of environmental laws banning or restricting PFSA, but still have many barriers before reaching commercial viability. PBI membranes are a more promising path, and are likely to take over the market in the near future given restrictions on PFSA.

Introduction

The fuel cell was invented in 1839 by Sir William Grove. Although the first prototype of a conceptual fuel cell design was able to harness the energy of hydrogen and oxygen, it was not able to produce much electricity – it would take a long time until the fuel cell was powerful enough for any real world applications (History - FuelCellsWorks, n.d.) [1]. Nevertheless, it was still a big breakthrough and a huge step in power generation technology. Over a century later, in the 1960s, the first proton-exchange membrane fuel cell (PEMFC) was developed by Thomas Grubb and Leonard Niedrac [2]. This prototype PEMFC needed a lot of refining, and one of the first developments that surfaced was a new membrane. Nafion™, developed by DuPont in 1962, pushed the PEMFC into the commercial world, allowing it to be used in places such as the NASA Gemini Program (1961-1966). As of today, PEMFCs are the most widely used type of fuel cell, typically more so in transportation applications.

Fuel cells work by combining a fuel and an oxidant, generally hydrogen and oxygen, although other gases may also be included. Hydrogen enters through the anode, while oxygen enters through the cathode. On the anode, diatomic hydrogen gas is split into protons and electrons. The protons pass through the membrane, while the electrons pass through a wire to induce an electric current [3]. The half-reaction on the anode can be represented by the equation:

$$2H_2 \rightarrow 4H^+ + 4e^-.$$

On the cathode, the oxygen gets reduced into water as it gains electrons and combines with hydrogen cations, or protons. The protons travel from the anode to the cathode via the electrolyte membrane, while the electrons travel to the cathode through an external circuit, powering a load. The half-reaction on the cathode can be represented by the equation:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O.$$

The overall reaction equation can be derived by adding the two half-reaction equations together [4,5], yielding:

$$2H_2 + O_2 \rightarrow 2H_2O.$$

This clean byproduct makes hydrogen fuel cells very appealing – having a clean energy source that generates water seems like a technology of the future.

One of the first mechanisms in the fuel cell that scientists looked to improve was the membrane. Acting as an electrolyte for the fuel cell, the polymer electrolyte membrane (PEM) allows protons to pass while also acting as a separator between the two electrodes. The two terminals of the fuel cell are separated by a membrane, keeping the contents of each terminal to themselves. Electrons are not able to short the circuit because of the presence of a membrane, and gases have limited transport through the membrane. Because the membrane directly impacts the energy density and efficiency of the fuel cell, a more efficient membrane would be able to improve proton conductivity and operate under a variety of conditions.

The most common PEM membrane in use today is the PFSA membrane. Nafion™ ionomers are the most common of these PFSA membranes [6], and they are considered the best membranes currently used. These state-of-the-art membranes are extremely chemically, thermally, and mechanically stable and have high ion conductivities [3], making them perfect for a broad range of applications. However, PFSAs also have their limitations. Namely, they have a relatively high cost and have a limited ion conductivity at temperatures over the boiling point of water [7]. Most importantly, however, the perfluorinated substances used to make the PFSAs are toxic to both humans and the environment, leading policy makers to start banning these compounds. Most recently, the EU has proposed a ban on perfluorinated substances including PFSA, prompting researchers to look for alternatives [8].

These alternatives come mainly in the form of two overarching types of membranes: Polybenzimidazole (PBI) membranes, and hydrocarbon-based membranes. Recent developments, mainly in PBI membranes, have even started to increase the viability of these membranes over PFSA membranes. Advances in these membrane technologies could replace the current PFSA membranes in many places and extend PEMFC applications beyond existing ones, allowing us to bring a clean, hydrogen-based future to reality.

In this paper, we will explore the different types of membranes used in PEMFCs, followed by their advantages, properties, and constraints. We will then discuss the recent developments and applications of the membranes, and conclude with a personal standpoint on where the membrane market is headed.

Proton-exchange membrane chemistry

PFSA

As shown in Figure 1, PFSA membranes have three main parts: the polytetrafluoroethylene (PTFE) backbone, perfluoroether side chains, and sulfonic acid ion clusters.

The backbone has a formula of $(C_2F_4)_x$, with the exception of a dropped fluorine atom at every site of a side chain attachment ($CF_2 \rightarrow CF$). They provide the main source of stability within the entire membrane, and are extremely hydrophobic, contributing to the phase segregation of PFSA membranes [9].

The side chains are perfluoroether side chains that vary in length – the length of these side chains determines whether the PFSA membrane is classified as long-side chain (LSC) or short-side chain (SSC) PFSA membranes. Both long-side and short-side chain PFSA membranes have the same base component of $(O - CF_2 - CF - O - CF_2 - CF_2)_x$, but membranes with three or more repeating units of this group are generally considered LSC PFSA membranes.

The hydrogenated sulfonic acid groups (SO_3H) cap these side chains off. These sulfonic acid groups are able to uptake water from their environment, creating a clear phase segregation between the hydrophilic sulfonic acid groups and the hydrophobic PTFE backbone [10]. The sulfonic acid groups are crucial for ion conductivity, especially when hydrated, as hydrogen ions are able to move around between the sulfonic acid groups and bond with water.

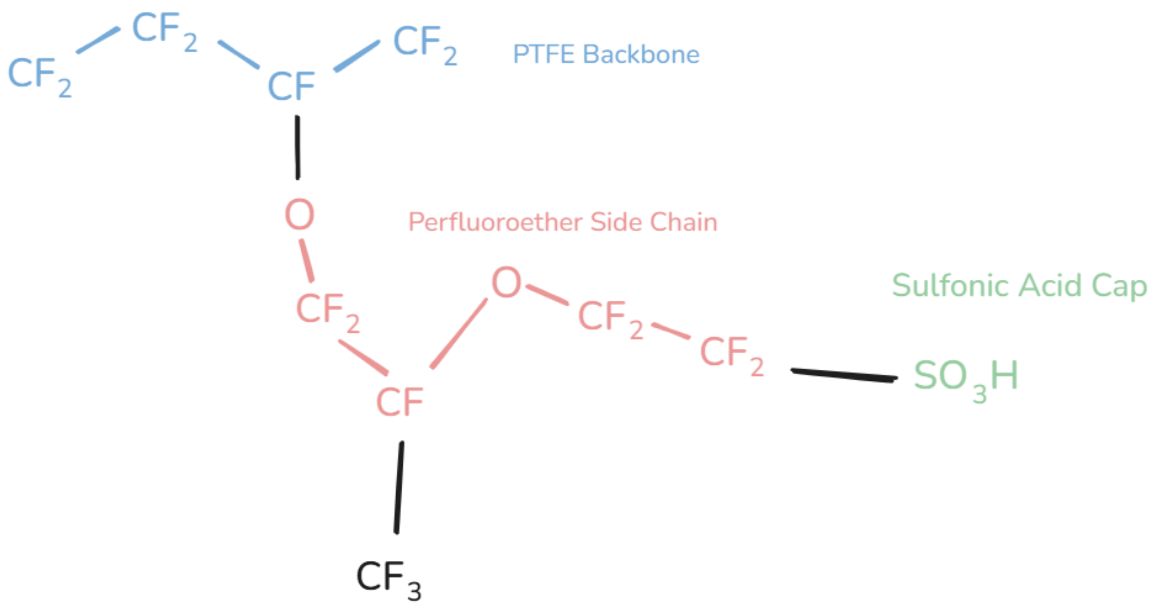

Figure 1: Basic Unit of a PFSA membrane

PFSA membranes are well-suited for fuel cells due to their unique combination of properties. The hydrophobic PTFE backbone with hydrophilic sulfonic acid ion clusters allows PFSA membranes to retain water efficiently, which supports high proton conductivity even at relatively low temperatures. With high proton conductivity at low temperatures, high mechanical, chemical, and thermal stability, and low gas permeability, it seems that PFSA membranes suit many general applications for fuel cells.

However, these properties tend to be extremely temperature dependent. As temperature increases, we see a downwards trend in most properties, as conductivity, stability, and durability all drop. The increase in temperature leads PFSA membranes to be much stiffer, leading mechanical properties of the membrane to become worse [11].

Just like temperature, an increase in relative humidity decreases the mechanical properties of PFSA membranes. Figure 2 shows how Young's Modulus (a measure of stiffness, which correlates to other properties) decreases dramatically as PFSA heats up to operational temperatures.

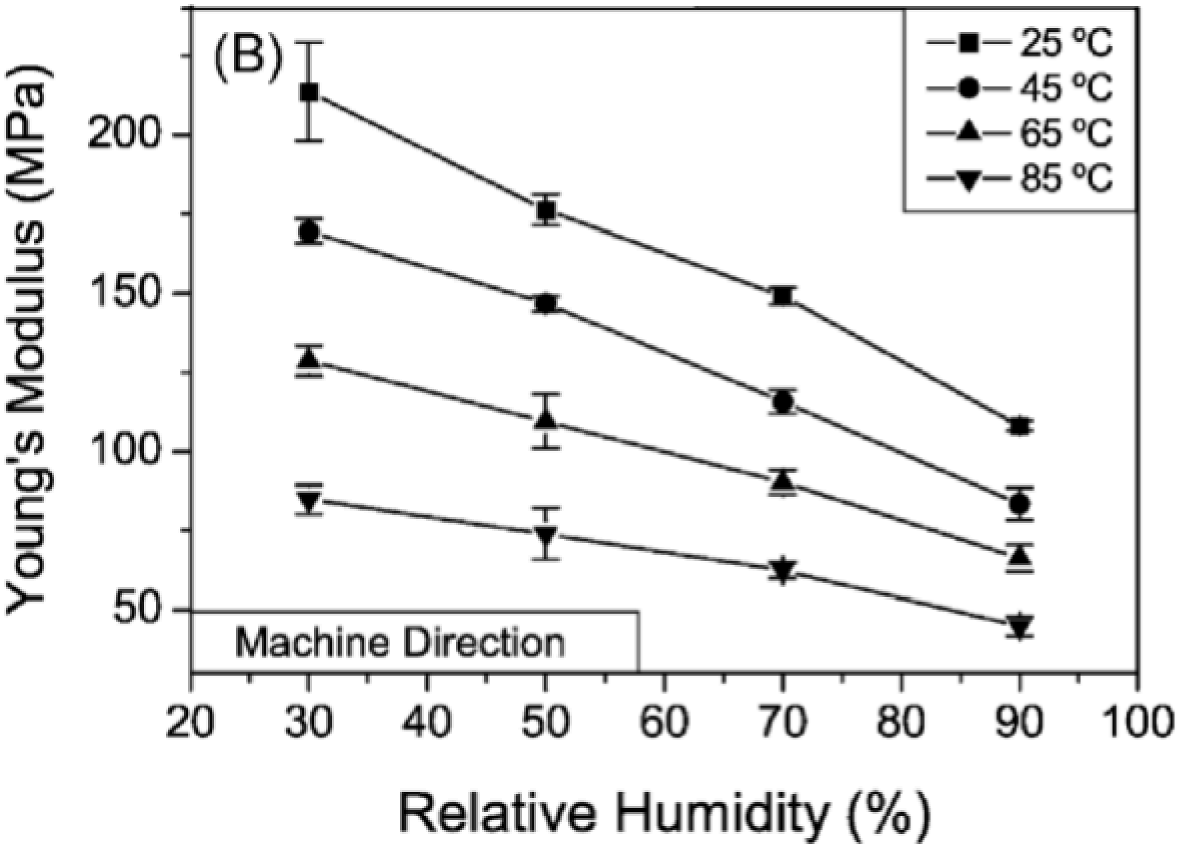

Figure 2: Young's Modulus vs. Relative Humidity and Temperature of Nafion 112 membrane, 100mm x 10mm x 0.05mm. [11].

The proton conductivity of a PEMFC depends on its membrane's ability to stay well-hydrated, as hydration allows protons to move through sulfonic acid sites. Currently, Nafion^{TM}, which is the leading PFSA membrane as of now, offers a high proton conductivity of 0.13 S/cm at a temperature of 75^{o}C [5].

However, even though the proton conductivity is more than enough to sustain commercial mass production, PFSA membranes must strike a balance of durability and conductivity by varying temperature. Under a temperature of 70 degrees Celsius, the ultimate strength of PFSA membranes drops to around 12.5 MPa down from around 20 MPa at room temperature [12]. This naturally limits the applications where PFSA membranes can be used, especially in higher operational temperatures.

Hydrocarbon-based membranes

Hydrocarbon-based membranes are a class of proton exchange membranes built on a full hydrocarbon backbone, as their name suggests. Common backbones of these membranes include polystyrene $(C_8H_8)_x$, polyphenylene $(C_8H_8O)_x$, and polyarylene $(C_2H_4)_x$, each of which offers slightly different properties depending on the application. These backbones are sulfonated, a process where sulfonic acid groups are added to the aromatic rings. This sulfonation introduces hydrophilic regions into the otherwise hydrophobic polymer, allowing proton-conducting channels to form. Figure 3 shows the basic structure of a hydrocarbon–based membrane, SPI, which is one of the most common types of hydrocarbon membranes.

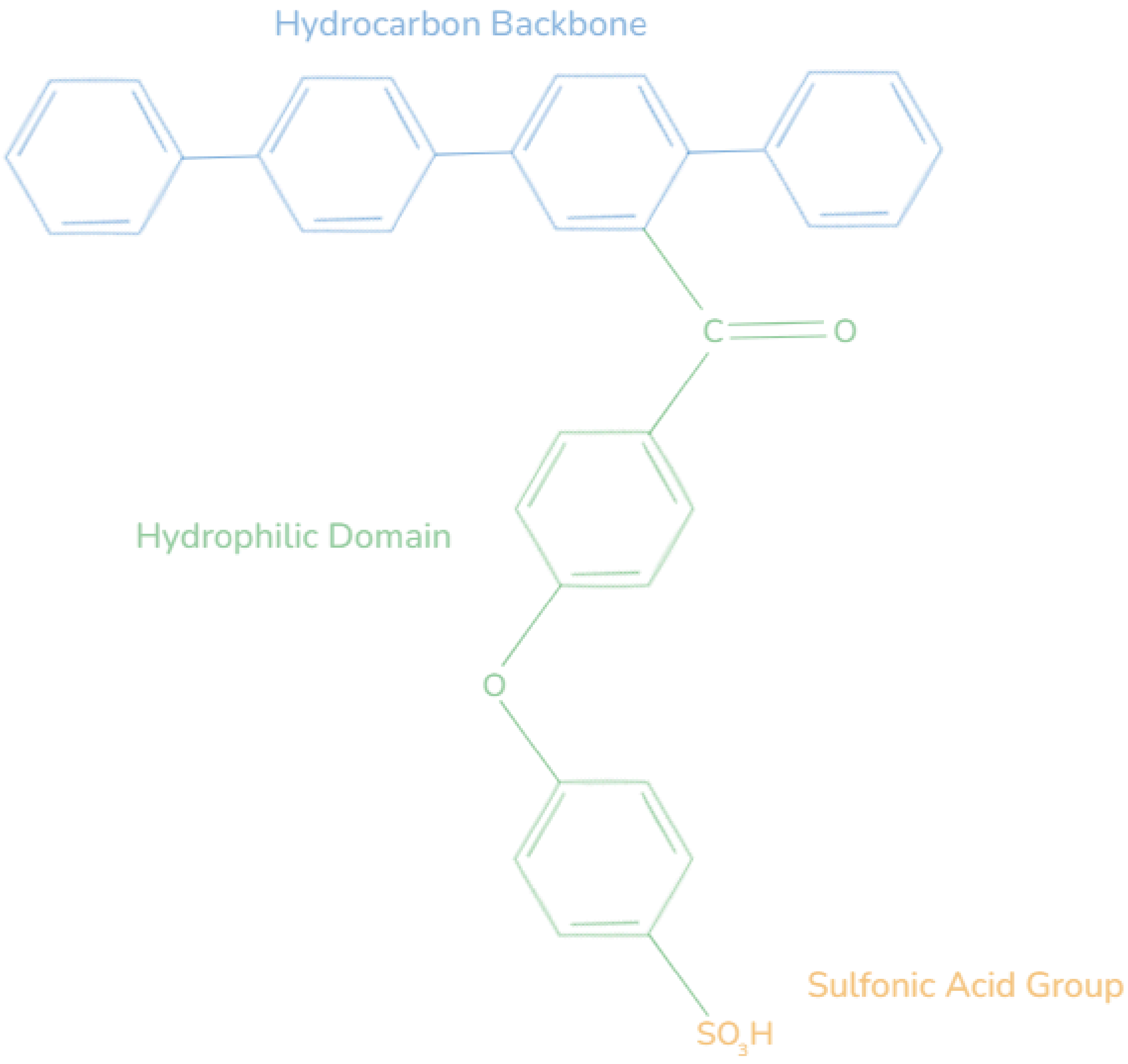

Figure 3: Structure of SPI (sulfonated polyimides), a hydrocarbon-based membrane

Hydrocarbon-based membranes are phase segregated, with a clear separation between the hydrophobic backbone and the hydrophilic sulfonic acid groups. This arrangement creates pathways for proton transport, similar to PFSA membranes. However, the rigid aromatic backbone provides increased mechanical stability and durability compared to the PTFE backbone of PFSA membranes. This added stability allows hydrocarbon-based membranes to be more robust in certain conditions, especially when exposed to mechanical stress or high-temperature environments.

In hydrocarbon-based membranes, protons are able to move through the hydrophilic regions of the sulfonic acid groups and absorbed water. These membranes rely heavily on hydration to maintain conductivity – fluctuations in humidity can greatly affect the mechanical properties of the membranes. However, to achieve conductivity comparable to PFSA membranes, hydrocarbon-based membranes require a much higher ion exchange capacity (IEC), which is a measure of the concentration of ion conducting groups per unit weight of the membrane. This increased IEC can lead to challenges such as excessive swelling at high humidity levels [13], which compromises mechanical stability.

Hydrocarbon-based membranes, being made with cheap hydrocarbons and inexpensive fluorine, seem great for applications where cost is most important. Hydrocarbon-based membranes also have a high mechanical and thermal stability, so they work well in harsher settings that require resistance to wear and tear [13].

While hydrocarbon-based membranes uptake water in a similar way to that of PFSA membranes, their hydration behavior is much more volatile than PFSA membranes, especially when relative humidity (RH) changes. At high RH, the membranes swell, which can enhance conductivity but also risk mechanical deformation. At low RH, dehydration leads to a sharp drop in conductivity, reducing the usefulness of the membrane in these conditions [13].

PBI

PBI, or polybenzimidazole membranes, are amorphous thermoplastic polymers. At the atomic level, PBI membranes are chains of benzimidazole ($C_7H_6N_2$) linked together. With strong hydrogen bonds, the structure of PBI is extremely rigid. Figure 4 shows the basic unit of a PBI membrane, doped with phosphoric acid (H_3PO_4).

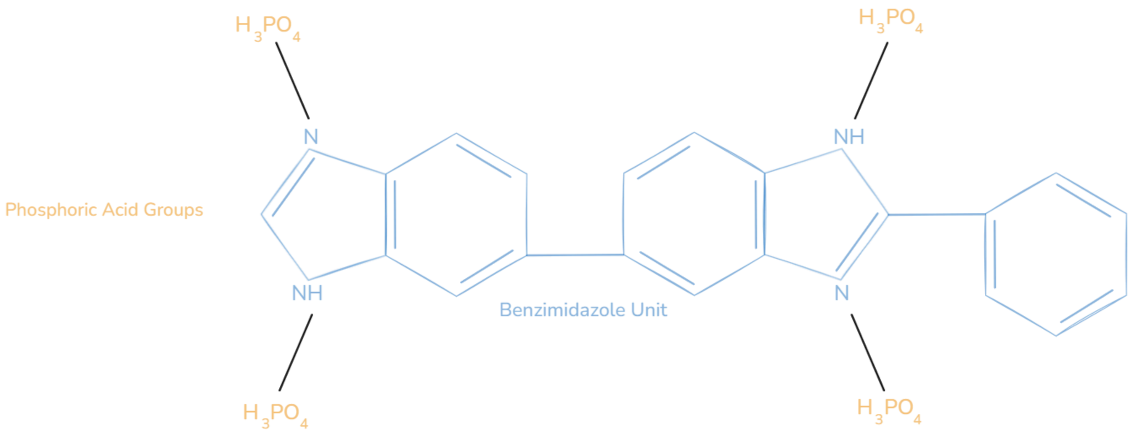

Figure 4: Basic Unit of a PBI membrane

Unlike PFSA membranes, unmodified PBI membranes do not conduct protons well. However, to solve this, PBI membranes can be doped with phosphoric acid to increase the proton conductivity.

When the membrane is doped, the acid molecules interact with the nitrogen atoms in the benzimidazole rings, allowing protons to move through the membrane. This allows PBI membranes to run more efficiently, especially at higher temperatures (150-200 degrees Celsius) [14]. Figure 5 shows data on the relationship between the doping level of PBI membranes with phosphoric acid and the conductivity level at 25C (circles) and 150C (squares). In fact, a higher doping percentage in the membrane is able to significantly increase the proton conductivity of the membrane. At 450 mol% phosphoric acid, PBI membranes are able to reach a maximum proton conductivity of 0.05 S/cm at 165 degrees Celsius. When that concentration increases up to around 1500 mol% phosphoric acid, PBI membranes reach the same level of conductivity as PFSA membranes at 0.13 S/cm. Judging solely on the proton conductivity, this would theoretically make these membranes much more, if not fully, commercially viable.

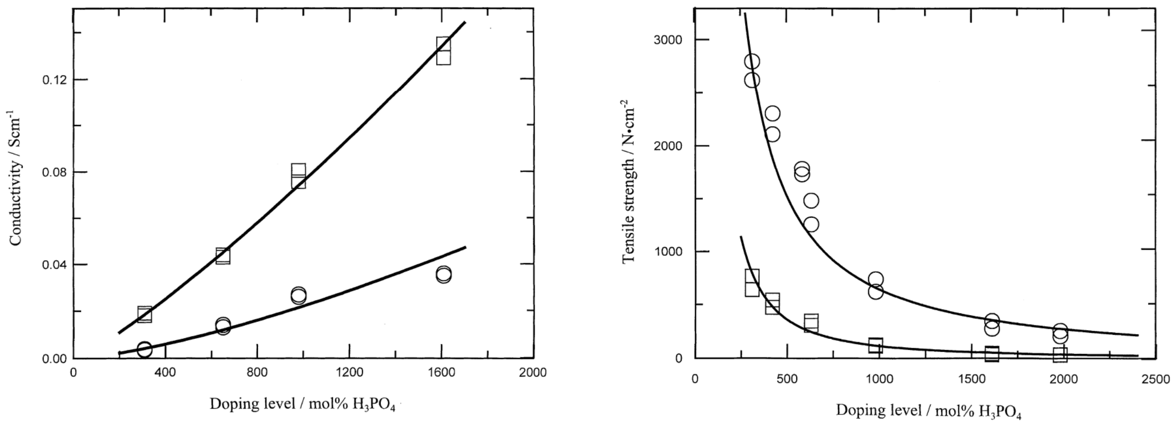

Figure 5: Conductivity, Tensile Strength vs Doping Level of H_3PO_4 for PBI Membranes. Circles are data points taken at 25C, and squares are data points taken at 150C. [14]

Unfortunately, one extremely weak point of PBI membranes is their durability. While adding phosphoric acid does increase proton conductivity, at the same time, it lowers the tensile strength of the membrane. At operational temperatures, there is more than a two-fold decrease from the tensile strength of PFSA membranes, dropping from 15 MPa for Nafion^{TM} to 6 MPa for PBI membranes [14].

This conductivity-durability tradeoff is the main limiter for commercial viability and considerably reduces the range of applications that PBI is able to be used for.

The reliance of PBI membranes on phosphoric acid doping introduces several other challenges, including acid leaching and temperature sensitivity. Over time, the acid is able to leach out of the membrane, reducing proton conductivity and shortening the operational lifespan – during shutdown of the fuel cell, condensed water leads to acid leaching [15]. The phosphoric acid tends to leak out the most at temperatures over 100 degrees Celsius, which includes the temperature range of optimal operation. As for temperature sensitivity, while PBI membranes perform well at high temperatures, their conductivity drops in colder environments, where the acid and protons aren't able to move as freely due to being in a lower energy environment. This limits their versatility compared to PFSA membranes.

Graphs for Comparison

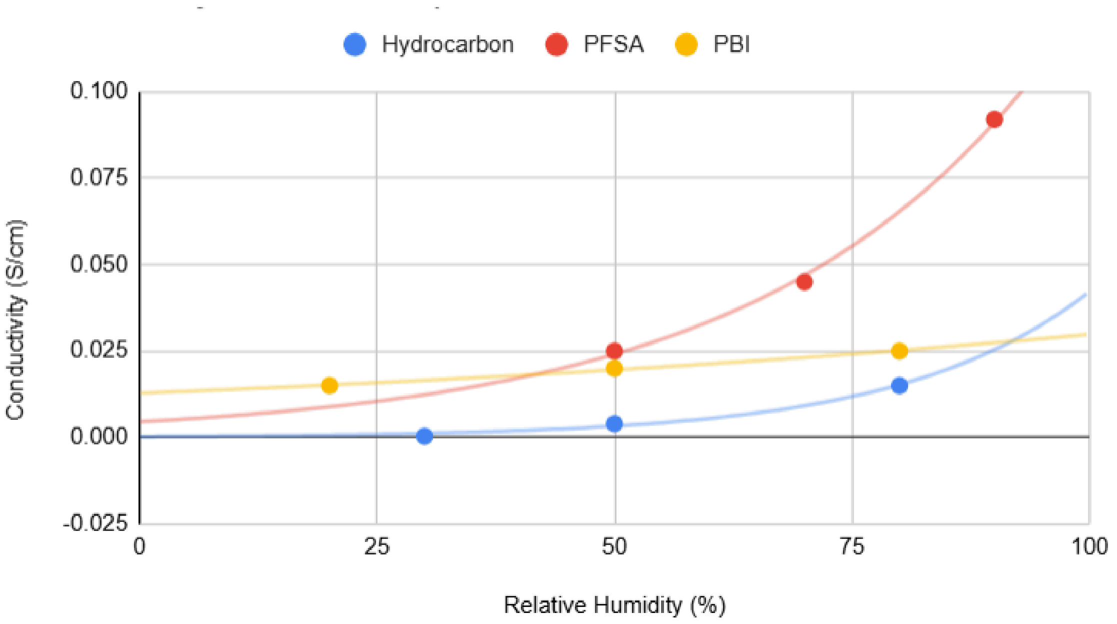

Figure 6: Conductivity vs. RH Comparison for PFSA (red circles), Hydrocarbon (blue circles), and PBI (yellow circles) membranes. Lines are polynomial fits through data.
(Data collected from Lee, et al. (2015), Guan, et al. (2023), Wang, et al. (2011). Used Nafion 117 (PFSA), SPES-50 (Hydrocarbon), PBI at a H_3PO_4 doping level of 5.6. (PBI). All data points taken at 80C.)

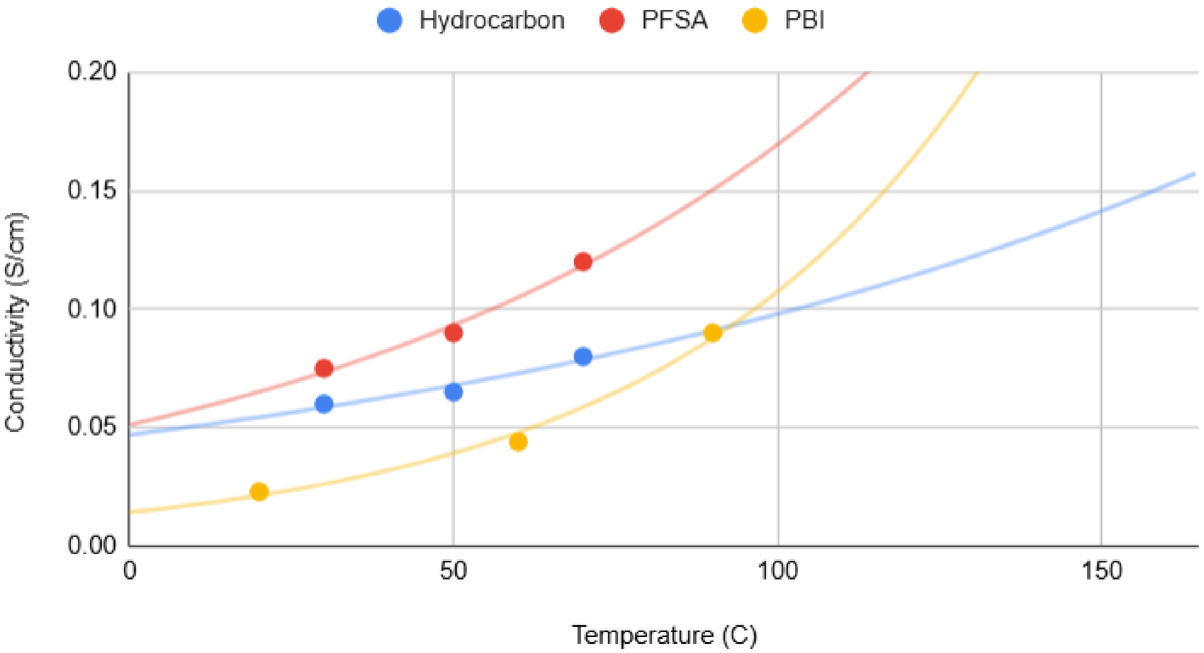

Figure 7: Conductivity vs. Temperature Comparison for PFSA (red circles), Hydrocarbon (blue circles), and PBI membranes (yellow circles). Lines are polynomial fits through data. (Data collected from Wang, et al. (2011), Ponomarev, et al. (2023). Used Nafion 117 (PFSA), SPAES-30 (Hydrocarbon), PBI-OMe at 85 wt% H_3PO_4 (PBI). All data points taken at 100% RH (fully hydrated conditions).

Discussion

To perform successfully in fuel cells, membranes must meet several requirements. They need high proton conductivity (around 0.1 S/cm) to enable efficient proton transport and facilitate the fuel cell's electrochemical reactions. Additionally, the membrane must have a low gas permeability to maintain efficiency and prevent gas crossover, which could disrupt reactions within the cell. The membrane must also be extremely durable to be able to withstand environmental conditions for a considerable amount of time (4000-8000 hours) [16]. Generally, PFSA membranes are particularly well-suited for these requirements, as they provide high proton conductivity along with high durability, giving it an edge over both hydrocarbon-based and PBI membranes. However, in specific cases, PFSA membranes may be outclassed by other types of membranes, as each application has its own constraints and operational conditions.

Of the many thousands of applications of fuel cells in powering systems, we can filter most of them down to just two categories: automotive power systems and portable power systems. Automotive fuel cells are used in cars, trucks, trains, and other heavy-duty transport applications, providing a stable and efficient source of energy. Portable power fuel cells, on the other hand, are used in places such as power tools and battery chargers, as lightweight and reliable power sources.

In automotive power systems, efficiency, durability, and high power output are primary requirements. Durability is the main requirement, followed by high power, as vehicles need to perform well even with considerable load changes as vehicles move around [17]. Membranes for automotive applications must also be able to withstand vibration and mechanical stress. High thermal stability is also crucial, as automotive fuel cells often operate in higher temperature conditions. While there are generally cooling systems in place, internal temperatures can reach upwards of 100C. Engines work well in these conditions, as increasing temperature increases efficiency (to an extent). Therefore, materials like membranes in fuel cells need to withstand these high temperatures without degrading. Prolonged exposure can lead to mechanical creep, which affects their durability and performance [18]. Therefore, maintaining high thermal stability and effective cooling is essential for the longevity and efficiency of automotive power systems, so that they can perform reliably under a variety of conditions.

For automotive power systems, PFSA membranes are the best option out of the three due to their high proton conductivity and durability. These membranes effectively facilitate the electrochemical reactions necessary for powering vehicles, making them well-suited for the demanding conditions of automotive applications. Their ability to withstand vibration and mechanical stress [11] is crucial, as vehicles experience significant movement and load changes. In Figure 6, we can see that all three membranes have an upward trend of conductivity as we increase RH. This is due to the fact that more water is absorbed at higher relative humidity values, which naturally leads to a higher conductivity. In Figure 7, again, we see an upward trend for all three membranes - the higher temperature allows for increased ion mobility, which increases conductivity. We can see that PFSA has higher conductivity than both hydrocarbon–based and PBI membranes at most temperatures and RH values. However, at higher temperature conditions, hydrocarbon membranes may become viable, especially as regulations against PFSA ramp up. They also have high mechanical strength under these conditions – the trouble is when brought outside of these conditions, the membrane starts to weaken and does not work as well [13]. Further developments are needed that either increase the conductivity of hydrocarbon-based membranes or reduce the operating challenges of using the membrane in a PEMFC.

For PBI membranes, which have a conductivity level similar to that of PFSA when doped, they have a much lower tensile strength at the same conductivity level, due to the huge tradeoff between conductivity and durability that PBI membranes experience when doped [14]. However, at higher temperatures, these membranes may become more suitable, as their conductivity approaches that of PFSA. Overall, while not perfect, PFSA still remains a more viable option than both hydrocarbon-based and PBI membranes, due to the fact that hydrocarbon-based membranes are extremely sensitive to temperature and PBI membranes become extremely weak when doped with acid.

In portable power systems, size, and weight are the main requirements. Portable power applications, like in laptops, drones, or mobile power stations, rely on fuel cells that are compact, lightweight, and able to deliver enough energy to power small appliances. Membranes in portable power systems must provide steady performance without bulky systems, as these would increase the device's size and weight. Ideally, portable power systems would operate at lower temperatures than automotive power systems, so they would use fuel cells with lower optimal working temperatures. Portable applications have lower power requirements such that lower power outputs can still be commercially viable, so power output is not considered as much as other factors.

For portable power systems, the differences between the three are less visible. Portable power systems operate at lower temperatures and lower relative humidities, which gives both hydrocarbon–based membranes and PBI membranes a fair chance at becoming viable for these systems. PBI membranes function well at low–humidity environments but only moderately well at low temperature environments, while hydrocarbon–based membranes function well at low temperature environments but not at low–humidity environments. Arguably, PBI membranes are the most promising type of membrane among the three discussed, as PBI membranes are much more consistent in their conductivity with fluctuating conditions than both PFSA and hydrocarbon–based membranes. Since strength is also less of a concern in portable power systems than automotive power systems, PBI membranes seem to be a very viable option over hydrocarbon–based membranes. While PFSA fuel cells are currently the best performing, the future for PFSA is being taken into question largely due to new regulations concerning PFAS (perfluoroalkyl and polyfluoroalkyl substances).

Because of the environmental effects of PFSA, it may soon be banned in many places around the world. Notably, Europe has started to make progress on a universal ban on perfluoroalkyl substances [8], which are involved in the production of PFSA membranes and are present within the structure of PFSA. As the ban slowly progresses, businesses, companies, and entire industries may start to look for alternatives, possibly in the form hydrocarbon-based membranes or PBI membranes. This shift will drive innovation in the fuel cell sector, prompting research into more sustainable materials that do not compromise fuel cell performance.

While PFSA is tentatively better than both PBI and hydrocarbon-based membranes, we have also spent most of our time optimizing PFSA membranes instead of looking into other alternatives. With the current bans on PFSA and prospective limitations on hydrocarbons in the near future, it is clear that we must look into cleaner yet more powerful alternatives for fuel cell membranes. We do not know yet the full potential of these membranes, especially PBI, and further research may lead to a huge shift in the way we power our world. PBI membranes have unique capabilities that give them a lot of potential, but they are not yet at the point where they fulfill the requirements to generate power reliably.

Conclusion

PFSA membranes remain dominant in automotive applications due to their high conductivity, durability, and mechanical strength, though hydrocarbon membranes may be viable at elevated temperatures. In portable power systems, where size and stability matter most, PBI membranes show promise due to their consistent conductivity under fluctuating humidity conditions, even with a lower mechanical strength. However, environmental concerns and stricter regulations may lead to a shift toward alternative membranes. Future advancements should focus on improving hydrocarbon and PBI membranes to increase the durability, conductivity, and stability required for widespread fuel cell adoption.

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