

## COB-2023-1828

# COMPARATIVE ANALYSIS OF PROTON EXCHANGE MEMBRANES AND ANION EXCHANGE MEMBRANES FOR LOW-TEMPERATURE FUEL CELLS

### Fábio Furtado

#### Matheus Ben-Hur Ramirez Sapucaia

Federal University of Paraná  
Graduate Program in Mechanical Engineering at UFPR - (PGMEC)  
Polymers Laboratory (LaPol) and Fuel Cells Laboratory (LaCelC)  
Sustainable Energy Research and Development Center - (NPDEAS)  
fabio.furtado@ufpr.br  
ben-hur@ufpr.br

### Beatriz Jacob Furlan

Federal University of Paraná  
Graduate Program in Materials Science and Engineering at UFPR - (PIPE)  
Fuel Cells Laboratory (LaCelC) and Sustainable Energy Research and Development Center - (NPDEAS)  
beatrizfurlan@ufpr.br

### Rodrigo César Raimundo

Federal University of Paraná - (UFPR)  
Graduate Program in Mechanical Engineering at UFPR - (PGMEC)  
Fuel Cells Laboratory (LaCelC) and Sustainable Energy Research and Development Center - (NPDEAS)  
rodrigo.cesar@ufpr.br

### José Viriato Coelho Vargas

#### Thais Helena Sydenstricker Flores-Sahagun

Federal University of Paraná - (UFPR)  
Department of Mechanical Engineering at UFPR - (DEMEC)  
Polymers Laboratory (LaPol) and Fuel Cells Laboratory (LaCelC)  
Sustainable Energy Research and Development Center - (NPDEAS)  
viriato@ufpr.br  
thaishelena@ufpr.br

**Abstract.** *In the context of increasing global energy consumption demand, it is necessary to search for alternative sources of energy that are clean, renewable, and mitigate negative environmental impacts, particularly in relation to the emissions of greenhouse gases such as methane and carbon dioxide. In this context appears the fuel cells that use hydrogen as the main fuel and have only energy and water as a product of their chemical reaction. This study aims to provide a theoretical overview of the main differences between proton exchange membrane fuel cells (PEMFC) and anion exchange membrane fuel cells (AEMFC), as they are the most promising for multiple applications. Fuel cells can be applied in stationary or portable equipment, such as electric vehicles, and can be one of the solutions for replacing combustion engines. This literature review aims to compare the main characteristics employed in each type of fuel cell, both proton exchange membrane and anion exchange membrane, with the aim of comparing their operations, preparation methods, chemical and physical characteristics, advantages and disadvantages, applications, and limitations. The membranes, whether proton exchange or anion exchange, are seen as essential components for the fabrication of fuel cells, as they directly influence the redox reaction by allowing the passage of protons or anions from one electrode to another, thus generating electric energy as a product. However, contamination or drying that often occurs in these types of membranes affects their efficiency and performance. To improve proton or anion conductivity, alternative polymeric materials to Nafion are often doped with phosphoric acid, but this reduces their mechanical strength. To solve this problem, researchers propose using reinforcements such as particles, nanoparticles, fibers, nanofibers, and others. However, anion exchange membranes using KOH suffer from carbon dioxide contamination. Therefore, it is important to understand the operating mechanisms of these two mentioned fuel cell types and analyze their prospects for improvement in research and development.*

**Keywords:** *polymeric membranes, chemical modification, reinforcements, proton conductivity, anion conductivity*

## 1. INTRODUCTION

The world population reached the number of 8 billion inhabitants in 2022 according to more recent data from the UN (2022) and, it estimates that in 2037 it will reach 9 billion people. This impact is an increase of over 56% in the consumption of world energy in the next thirty years (Masnadi et al., 2014). The global system of energy consumes a great number of resources, which can be finite, such as fossil fuel, or renewables, such as biomass (Speirs et al., 2015). Conservation, efficiency, implementation of technology, and production of renewable energy are preoccupations that are pointed out in this system (Rosenberg et al., 2013). Among the energy sources, one of them is the fuel cell, which is an energy source of low environmental impact that converts chemical energy directly into electrical energy (Bose, 2018). One of the possible fuels that can be used in a fuel cell is hydrogen gas ( $H_2$ ). Systems of energy that use hydrogen contribute to the resolution of problems related to air pollution (Jin et al., 2022; Liu et al., 2022; Zhu et al., 2022). Therefore, fuel cells mitigate environmental impacts because they do not emit gases which are caused by the greenhouse effect, which could affect the air quality, once they have products their chemicals are water, electric energy, and heat (Merle et al., 2011).

In a proton exchange membrane, the hydrogen enters the anode and causes an oxidation reaction, with a division in hydrogen cations and electrons ( $H_2 \rightarrow 2H^+ + 2e^-$ ). These electrons follow the external circuit producing electrical energy by an external charge and arrive at the cathode to participate in the oxygen reduction process ( $1/2O_2 + 2e^- \rightarrow O^{2-}$ ). The produced oxygen anions migrate from the cathode to the anode, undergoing the electrolyte, end the cycle, and obtaining an electrochemical general reaction with the production of electrons and water such as product ( $2H^+ + O^{2-} \rightarrow H_2O$ ) (Fan et al., 2022). In an anion exchange membrane, the hydrogen gas carried out in the anode reacts with the hydroxyl anions and, consequently, generates water and electrons ( $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$ ). Electrons are transferred by an external circuit until the cathode, in which the oxygen reacts with the water to generate hydroxyl ions ( $2e^- + 1/2O_2 + H_2O \rightarrow 2OH^-$ ). As a general reaction, molecules from hydrogen gas react with an oxygen molecule to generate products, such as water, electrical energy, and heat (Merle et al., 2011). Figure 1 presents schematic representation of PEMFC and AEMFC.

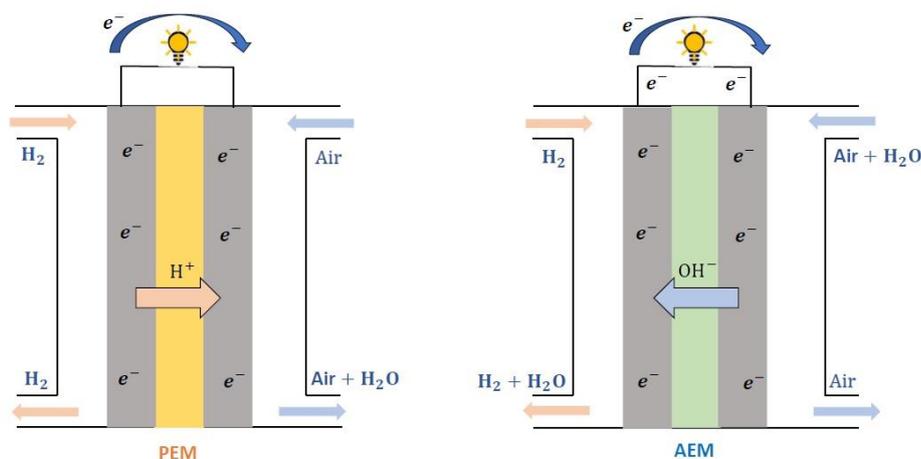


Figure 1. Schematic representation of PEMFC and AEMFC.

## 2. PROTON EXCHANGE MEMBRANE

The proton exchange membrane fuel cells (PEMFCs) have a polymeric membrane. This polymeric membrane has several organic compounds with functional groups of proton exchange, which usually is used with a sulfonic group. The PEMFCs can be used in portable equipment, aviation, automobiles, ships, and systems of stationary power (Prykhodko et al., 2021; Wu; Chiou, 2021). The PEMFC is considered a system of conversion of energy of low environmental impact which proportionate properties favorable such as fast start, high density of power, and efficiency (Jin et al., 2022).

The proton exchange membrane is considered the core of the PEMFC and its main function is to serve as a solid electrolyte. The material most common in the manufacturing of the polymeric membrane is the Nafion, whose material is registered by DuPont. The Nafion is a membrane of perfluorosulfonic acid, whose proton conductivity depends on the presence of water for proton solvating. The Nafion membrane operation temperature is limited below 100 °C, usually between 50 and 90 °C at room pressure. Thus, fuel cells based on Nafion are named low-temperature PEMFCs (LT-PEMFCs). They require the use of hydrogen extremely pure, once even small traces of carbon monoxide led to contamination of the platinum catalyst used in the electrodes (Rao et al., 2019). Water is needed for the hydration of a

membrane of protonic conduction, however when a quantity of water is excessive, it could have blocks in the pores of the electrodes, and this results in swelling that could cause serious problems in the air passive diffusion (Dang et al., 2021). The Nafion in the hydrated state presents high values of protonic conductivity, but its range of operation temperature is below the water boiling point and its manufacturing is complex and relatively expensive (Jankowska et al., 2021).

The proton exchange membrane together with the catalyst layer and the gas diffusion layer make up the membrane electrode assembly. The hydrogen initially is decomposed into protons and electrons in the anodic catalyst layer. Subsequently, protons migrate through the proton exchange membrane towards the cathode, where they combine with oxygen for the oxygen reduction reaction, occurring in the so-called triple boundary phase. The gas diffusion layer, with its porous structure, plays a crucial role in the transport of reactants, products, electrons, and heat. Therefore, optimization of not only material selection, but also the triple boundary phase configuration, is essential to ensure proper transfer of reactants, protons, electrons, water, and the necessary reaction processes. (Fan et al., 2022).

Within membrane electrode assembly, the proton exchange membrane separates the reagents gases and leads the protons of the anode side to the cathode side. To obtain high protonic conductivity, the proton exchange in order to provide high performance requires thermal, chemical, and electrochemical stability, high strength enough for do not deform under loading, high capacity to separate gas, and competitive price. The perfluorinated membranes are the most common and the presence of fluoride atoms in the membrane chain ensures good chemical oxidation and mechanical stability (Prykhodko et al., 2021). A required proton exchange membrane should contain excellent chemical and thermal stability, high protonic conductivity, good mechanical properties, ease of manufacturing, low cost, satisfactory durability, and enough water uptake. The mechanism of proton conduction is related to the electrostatic interactions and proton solvation energy. It also is characterized by high protonic mobility and activation energy, once the hydrogen bond cleavage requires a loss of energy of about 0,11 eV (Zhu et al., 2022).

One of the materials cited to replace the Nafion in the manufacturing of proton exchange membranes is polybenzimidazole (PBI), which can be doped with phosphoric acid. The PBI modification to use in proton exchange membranes generates improvement in the PBI properties regarding conductivity, strength, or chemical stability. The PBI protonic conductivity increases with the increase of acid doping level, with the increase of concentration of phosphoric acid bath in which membranes are immersed. When PBI membranes are doped, greater acid content and lower strength are obtained. To solve this problem, it is customary to use inorganic fillers in the polymeric membrane, such as silica (SiO<sub>2</sub>), zirconia (ZrO<sub>2</sub>), or titanium dioxide (Pinar et al., 2012).

The thickness of the Nafion membrane plays an important role on charge and discharge stress, and time, in addition to determining the electrolyte cross-over and membrane strength. The Nafion is considered as a material of difficult replacement due to its better performance, such as good protonic conductivity, and excellent oxidative stability. However, the Nafion presents limitations, which can be solved by modification methods, as well as the reticulation, mixing, and introduction of fillers, such as hydrophilic inorganic materials, metalorganic parties, and ionic liquids. The development and application of novelties in the proton exchange membrane require a delicate balance between physical properties, compatibility of the membrane electrode assembly, electrochemical properties, cost, and durability (Zhu et al., 2022).

Aromatic polymers with pyridine and quinoline are alternatives to replacing Nafion membranes, in addition to polyolefinic polymers with repeating units of pyrrolidone and imine. In this case, membranes are considered high-temperature polymeric electrolytes. In addition, there are options for reinforced polymers based on quaternary ammonium, such as polysulfone (PSF), poly(arylene ether sulfone) (PAES), and poly(arylene ether ketone) (PAEK). There is still the possibility of the use of functionalized polymers with imidazole, which include the poly(epichlorohydrin) (PECH), poly(phenylene oxide) (PPO), and poly(vinyl chloride) (PVC) (Jin et al., 2022).

The conductivity is directly correlated with the number of donor protons and their mobility, both are a function of the temperature. Polarization curves of a PEMFC are divided into three parts: the first happens in low current densities that are governed by reactions that occur in the cell and is named for activation loss; in the second part polarization curves occur in densities of intermediate current, with the region governed by ohmic drop, responsible for the protonic mobility; The third and last part is marked for the drastic voltage drop when the current density increase and the region is governed by mass transfer. The ohmic resistance is directly correlated with the protonic mobility through the membrane and the ohmic drop is generalized by contacts and wires (Pinar et al., 2012). The protonic conductivity is calculated by equation (1):

$$[\sigma] = \{[L]/[A]\}\{1/[R_{\Omega}]\}, \quad (1)$$

Where  $[\sigma]$  is the protonic conductivity,  $[L]$  is the distance between two electrodes,  $[A]$  is the cross-section, and  $[R_{\Omega}]$  is the resistance (Ghosh et al., 2022).

The proton transport mechanism in a hybrid system depends on the chemical properties and surface properties of the interface between the organic and inorganic phases. The mechanical and physical properties of composite proton exchange membranes can be affected by low compatibility between Nafion and hygroscopic fibers. The membrane of the composite both retains the water and increases the capacity to absorb it. The water uptake capacity of the membrane

reinforced with silica is bigger than the recasting Nafion membrane and those from Nafion 112. The membrane reinforced with zirconia presents greater protonic conductivity if compared only with those from Nafion (Zhu et al., 2022).

For the performance and durability of PEMFC, the proton exchange membrane should be designed with high protonic conductivity, gas permeability, and good mechanical properties. The introduction of polymers can regulate the mechanical stability and the reagent gas permeability and contribute to the formation of the triple phase boundary, with the activation of sites for the oxygen reduction reaction. The binder content is a key factor of selection because if it is excessive, gas diffusion will be offside and if it is low, the ionic conductivity will be affected and more catalysts will be isolated with fewer reactive sites (Liu et al., 2022). Liu et al. (2022) cite as examples of binder polymers Nafion, PBI, poly(ether ether ketone) (PEEK), polyimide (PI), poly(ionic liquid) (PIL), polysulfate, and polyethersulfone.

Excellent chemical and physical stabilities and commercial availability are characteristics of the Nafion membrane reinforcements. For the hydrophilic nature of the inorganic reinforcements, membranes of composites of Nafion matrix reinforced with inorganic materials can easily keep water and show high performance at temperatures above 50 °C and relative humidity equal to or lower than 50%. The size of reinforced particles is obtained by the dispersion method, based on grinding of raw material, with sizes from 20 to 30 nm, or by condensation method, based on the deposition of nanoparticles obtained, with a variety of several nanometers. Hybrid membranes have the expectation of improvement in performance, durability, conductivity, and production on a large scale, in recycling and in industrial development that will engage in the future (Prykhodko et al., 2021).

### 3. ANION EXCHANGE MEMBRANE

Alkaline fuel cells (AFCs) have demonstrated high power densities and stability during operation, working at lower temperatures and with relatively higher efficiency compared to other types of fuel cells. They can achieve a considerable lifespan, making them a worthy competitor to proton exchange membrane fuel cells (PEMFCs) (Gottesfeld et al., 2018). AFCs were the first type of fuel cell to be used in practical applications, starting in the 20th century with NASA's Apollo space program and still being necessary for aerospace applications today (Merle et al., 2011).

In the early development of the fuel cell concept, the first fuel cell to be developed and used for engineering applications was an AFC with a liquid electrolyte solution of KOH for its operation. KOH has the highest conductivity among alkaline hydroxides. However, the solution was also very sensitive to the presence of CO<sub>2</sub> in the air, requiring strict control to allow only oxygen without contaminating gases to enter (Zheng et al., 2019). Due to this issue, solid and polymeric membranes were developed to improve AFC efficiency and reduce CO<sub>2</sub> contamination. However, this was not a permanent solution, which remains a disadvantage of AFCs and contributed to the growth and widespread use of PEMFCs (Gülzow, 1996).

The realm of alkaline fuel cells took a significant step forward with the introduction of anion exchange membrane fuel cells (AEMFCs) to replace traditional liquid electrolyte AFCs. Both types have similar energy generation characteristics, but AEMFCs require higher technological rigor for their operation and membrane manufacturing (Mustain et al., 2020 and Gottesfeld et al., 2018). The possibility of using a greater variety of solid membranes, catalysts, and current density brings great potential for new studies.

Over the years, PEMFCs have gained significant market traction due to their stable operation and established technology, providing confidence and safety in their use. However, in recent years, PEMs have started to face insurmountable obstacles, mainly due to the need for electrodes with a high noble metal composition. Gradually, research in low-temperature fuel cells has shifted towards AEMs, given the potential to work with membranes that offer improved ion conductivity and the advantage of reducing costs by utilizing electrodes made with less expensive metals while maintaining relatively higher efficiency.

AEM typically requires excellent hydroxide conductivity, and its physical and chemical properties greatly influence the performance and durability of the cells. A polymer electrolyte membrane is a key component in both fuel cells and flow cells. It consists mainly of charged polymers, the hydrophobic backbones of the polymer are used to maintain the structure of the membrane, and charged groups are used to construct hydrophilic ions transport channels (Huang, 2022).

With the possibility of mitigating CO<sub>2</sub> contamination in membranes and developing catalysts composed of non-rare metals, significant investments have been made in the development of new alkaline membranes that can withstand high temperatures, continuous ionic conductivity, and long lifespan. In agreement with Kalienkova (2021) the mechanism of ionic conduction in the membrane is highly consistent with that of the electrolyte solution, primarily relying on ion dissociation and free movement. Simultaneously, the hydrophilic region in the membrane acts as the ion conduction channel, which is necessary for its proper functioning.

The significant advantage of pursuing new research directions in AEMFCs is that this type of fuel cell offers higher current density and a wider range of catalyst utilization without the need for high-purity noble metals, thereby reducing production costs (Kang, 2021). Generally, AEMs are primarily composed of high molecular weight compounds, such as polymeric structures and cationic groups. The polymer backbone carries cationic groups and maintains the dimensional stability of the AEM, while the cationic groups serve as functional groups responsible for the transport of OH<sup>-</sup>. An ideal AEM should have the highest possible ionic conductivity while maintaining the dimensional stability of the membrane.

Unfortunately, the molecular structure of the membrane itself decomposes due to the presence of the highly nucleophilic OH<sup>-</sup> group. Increasing temperature, which is a common characteristic of fuel cells during operation, leads to a reduction in ion exchange capacity (IEC), conductivity, and mechanical strength. Currently, there are still challenges in developing a membrane that can maintain all its physical and chemical characteristics over long periods during the operation of an AEMFC (You, 2020 and Chen, 2021).

AEMs primarily face the following four technical challenges: insufficient alkali resistance, insufficient output power density, trade-off between properties of anion-exchange polyelectrolytes (AEPs), and ion conduction mechanism. Cationic functional groups are susceptible to attack and degradation by OH<sup>-</sup> ions in an alkaline environment. At elevated temperatures, such as 80°C, most cations, including quaternary ammonium, imidazole, and pyridine, among others, are easily degraded by OH<sup>-</sup> (Miyaniishi, 2016).

Indeed, aryl-ethers based on AEPs have shown limited performance in fuel cells and physical properties, leading researchers to shift their focus towards aryl ether-free AEPs. The backbone of a polymer material plays a crucial role in determining its solubility, mechanical properties, microphase separation ability, and flexibility. In recent years, researchers have recognized that the backbone also plays a vital role in the fundamental stability of AEPs (Long, 2021).

Quaternary ammonium, being the earliest developed and most cost-effective ionic group, continues to be widely used in AEM research. The degradation pathway and mechanism of quaternary ammonium cations in an alkaline environment have been extensively investigated by researchers. Typically, researchers connect quaternary ammonium cations to the polymer backbone using a long alkyl chain to stabilize the fundamental properties of the backbone (Chu, 2019).

Historically, in the early stages of AEM research, low-cost engineering plastics such as poly(ether ether ketone) (PEEK) (Zhang, 2019), poly(phenylene oxides) (PPO), and polysulfone were utilized (Oh, 2019). AEMs based on polyether polymers are achieved through backbone chloromethylation followed by amination. To this day, these materials still occupy a significant portion of the AEM domain due to well-established synthesis procedures and favorable yields. However, more recently, modified poly(arylene ethers) (PAES) and PEEK have been explored, introducing additional reaction sites on the monomer intermediates through premodification approaches. For instance, PAESDOME-x copolymers, which employ two phenolic hydroxyl groups to bridge the cations, exhibit an improved ionic conductivity of 76.1 mS/cm at 80°C (Xue, 2020).

#### 4. METHODOLOGY

This article results from a search of studies in the literature that investigate the characteristics of proton exchange membranes and anion exchange membranes. The studies analyze the proton or anionic conductivity, chemical and thermal stability, resistance, water absorption and permeability of these membranes. A comparative analysis between the results of different studies highlights their advantages and disadvantages.

Furthermore, this study focuses on examining specific aspects of each type of membrane, as well as their similarities, applications, and limitations, with the aim of identifying opportunities for improvement and innovation. It offers insights into areas where new developments can be made in parallel with current research, as well as areas with potential for improvement.

#### 5. RESULTS AND DISCUSSION

A total of 32 studies on PEMFC and 21 on AEMFC were examined to assess their advantages, limitations, and applications. For PEMFC, key advantages include a wide temperature range, lightweight design, flexibility, ease of operation, low noise, thermal stability (Nafion), and high permeability to water and cations. Limitations include voltage drop, unstable performance, concentration polarization, and various challenges in reactions. Many of these factors are related to the use of Nafion as a proton exchange membrane, which is effective at low temperatures but less so at high temperatures.

Table 1. Advantages, limitations and mean uses for PEMFC mentioned in different studies researched in the literature.

Advantages	Studies mentioned with PEMFC*	Limitations	Studies mentioned with PEMFC*	Uses	Studies mentioned with PEMFC*
Environment friendliness	19	Low temperature (Nafion)	15	Portable devices	15
High proton conductivity (Nafion)	14	High cost (Nafion)	15	Vehicles (cars, bus, ...)	13

High energy efficiency conversion	13	High relative humidity (Nafion)	14	Stationary power stations	12
Chemical stability (Nafion)	13	Susceptibility to catalyst poisoning by CO (Nafion)	10	Ships	6
High power density	9	Durability	4	Aviation	5
Quick start-up	8	Manufacture (Nafion)	3	Household appliances	1
Good mechanical strength (Nafion)	8	Recycling	2	Not mentioned	13
Compact design	4	Low stability of the membrane	2		
Others	12	Others	16		
Not mentioned	4	Not mentioned	4		

\* A detailed list of all referenced studies is available at the end of the paper.

Table 2 summarizes findings from 21 AEMFC studies, highlighting advantages like acid corrosion resistance, system robustness, low noise, and high power and energy density, along with fuel flexibility. Notable limitations include lower power density, water management challenges, electrode-related issues, and operational inadequacies.

Table 2. Advantages, limitations and mean uses for PEMFC mentioned in different studies researched in the literature.

Advantages	Studies mentioned with AEMFC*	Limitations	Studies mentioned with AEMFC*	Uses	Studies mentioned with AEMFC*
Use of non-precious metal catalysts	18	Low alkaline stability	12	Stationary power stations	7
Faster electrode kinetics	10	Low ionic conductivity	9	Portable devices	5
Environment friendliness	9	Lower efficiency than PEMFC	8	Vehicles (car, bus, ...)	5
Higher efficiency than PEMFC	4	Mechanical properties limited	7	Aviation	2
Efficiency energy conversion system	3	Low lifetime	5	Household appliances	2
Use of non-fluorinated compounds	3	Carbon dioxide poisoning	5	Ships	1
Reduce crossover of fuel	3	Low temperature	3	Storage energy systems	1
Durability in low temperature and compact design	2	Backbones vulnerable to nucleophilic attack by hydroxide ion	3	Installation Ruppertshain, and meteorological station	1
Others	13	Others	10	Water electrolysis	1
Not mentioned	1	Not mentioned	2	Not mentioned	11

\* A detailed list of all referenced studies is available at the end of the paper.

In comparison with Table 1 and 2, it becomes clear that the most prominent advantages of PEMFC are environmental friendliness, high Nafion proton conductivity, and high energy efficiency conversion. Conversely, AEMFC is distinguished by its use of non-precious metal catalysts, faster electrode kinetics, and environmental friendliness. Environmental friendliness is a common theme, reflecting the low-pollution and sustainable nature of fuel cell systems in general. While most studies favor PEMFC for energy efficiency, a few offers alternative perspectives, suggesting that fuel cells, in general, can outperform conventional energy production systems. Nafion, valued for its high proton conduction and stability, has limitations related to its low-temperature and high humidity requirements, cost, and vulnerability to CO poisoning. AEMFC's potential advantages include cost reduction through non-precious metal catalysts and faster electrode kinetics, driven by non-fluorinated compounds, as suggested by some studies. Nevertheless, AEMFC faces notable limitations, such as low alkaline stability, limited ionic conductivity, mechanical weaknesses, and a short lifespan, which are actively being addressed by researchers seeking innovative solutions, including alternative polymer choices, catalyst materials, and improved water and heat management systems.

Figure 2 reveals a notable difference in the number of articles published on AEMFC compared to PEMFC, indicating a substantial opportunity for advancements and discoveries in AEMFC technology. AEMFC studies are relatively recent compared to PEMFC, and new research in this field can significantly contribute to further understanding and improvement of this energy system. The growing trend in studies on both types of fuel cells (AEMFC and PEMFC) is visible in Fig. 2, mainly with the significant increase occurring between 2010 and 2020. While PEMFC studies began in 1991, AEMFC studies only began in 2007. Notably, in 2006, publications almost tripled about PEMFC compared to the previous year (2005). Therefore, research on AEMFC is still in the early stages of development, with the number of studies remaining below 200 per year.

To sum up, AEMFC studies are focused on improving performance by enhancing mechanical properties, ionic conductivity, extending the system's lifespan, and addressing carbon dioxide poisoning issues. The attractiveness of AEMFC lies in its potential to use non-precious metals as catalysts, leading to substantial cost reductions, and in employing low-cost polymer membranes for anion exchange. Researchers are actively seeking Nafion membrane alternatives to reduce costs. Significantly, many AEMFC studies do not specify their applications, with almost half of the surveyed articles focusing on exploring the advantages and limitations of anion exchange membranes. Some articles may omit details about advantages, limitations, or applications. Tables 1 and 2 accommodate studies covering multiple aspects. These advantages and limitations are subjects of extensive global research efforts.

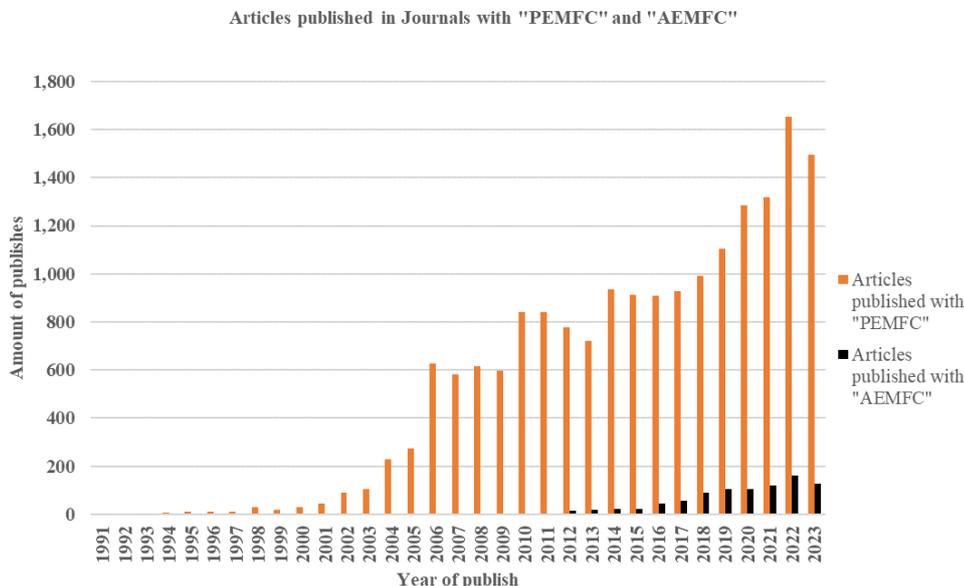


Figure 2. Graphic representation of PEMFC and AEMFC articles published over the years.

## 6. CONCLUSION

In this study, it was observed that proton exchange membranes (PEMs) and anion exchange membranes (AEMs) operate with different ion exchange mechanisms due to the distinctions in their structures. Both produce water and electricity from hydrogen and oxygen, but their individual characteristics influence possible applications and limitations, particularly in the context of mobile systems and prolonged use. AEMs offer higher current density and allow the use of high-purity noble metals, reducing costs compared to PEMFCs. This results in an increase in research

on AEMFCs. However, the lower durability of AEMs requires treatments to strengthen their structure and ensure long-term efficiency, which represents a significant economic challenge.

The development of membranes for PEMFCs has advanced considerably in recent decades, resulting in a greater amount of research compared to AEMFCs. This is since anion exchange membranes are a relatively recent area and still in the early stages of large-scale application. The focus in AEMFCs is improving their conductivity, while membranes for PEMFCs are designed to improve a combination of properties, covering economic, electrical, chemical, mechanical and durability aspects. There is a growing demand for polymeric membranes that replace liquid electrolytes in AEMs, aiming for long-term stability and efficiency, reducing costs, and expanding applications. In PEMFCs, there is an effort to replace Nafion membranes with other polyelectrolytes, diversifying materials and reducing manufacturing costs for electrodes with noble metals.

## 7. ACKNOWLEDGEMENTS

To the Brazilian National Council of Scientific and Technological Development - (CNPq) - [projects 405864/2022-1, 408073/2021-7, 408080/2022-1, 304440/2020-5, and to project 300093/2022]; CAPES; Ministry of Education (MEC), Brazil - (projects 062/14 and CAPES-PRINT-UFPR-88881.311981/2018-01); Araucaria Foundation of Parana, Brazil (project 115/2018, no. 50.579 – PRONEX), to FUNDEP, Renault and UFPR for the funding and the development of the project called “ROTA 2030”.

## 8. REFERENCES

- Abdi, Z. D., Chiu, T-H., Pan, Y-Z, Chen, J-C., 2020. “Anion exchange membranes based on ionic polybenzimidazoles crosslinked by thiol-ene reaction”. *Reactive and Functional Polymers*, v. 156, pp. 104719.
- Bayer, T., Cuning, B. V., Selyanchyn, R., Nishihara, M., Fujikawa, S., Sasaki, K., Lyth, S. M., 2016. “High temperature proton conduction in nanocellulose membranes: paper fuel cells”. *Chemistry of Materials*, v. 28, p. 4805-4814.
- Beauger, C., Lainé, G., Burr, A., Taguet, A., Otazaghine, B., Rigacci, A., 2013. “Nafion®-sepiolite composite membranes for improved proton exchange membrane fuel cell performance”. *Journal of Membrane Science*, v. 430, p. 167-179.
- Bose, A. B., 2018. “Composite membrane for polymer electrolyte membrane fuel cell”. Patent, United States Patent and Trademark Office, Registry number: US-9929410-B2, Application date: 21 August 2015, Publication date: 17 December 2015.
- Cai, Z., Li, R., Xu, X., Sun, G., Zhuang, X., Liu, Y., Cheng, B., 2018. “Embedding phosphoric acid-doped cellulose nanofibers into sulfonated poly(ether sulfone) for proton exchange membrane”. *Polymer*, v. 156, p. 179-185.
- Chen, N., Lee, Y. M., 2021. “Anion exchange polyelectrolytes for membranes and ionomers”. *Progress in Polymer Science*, v. 113, pp. 101345.
- Chu, X., Liu, L., Huang, Y., Guiver, M. D., Li, N., 2019. “Practical implementation of bis-six-membered N-cyclic quaternary ammonium cations in advanced anion exchange membranes for fuel cells: Synthesis and durability”. *Journal of Membrane Science*, v. 578, p. 239-250.
- Compañ, V., Escorihuela, J., Olvera, J., García-Bernabé, A., Andrio, A., 2020. “Influence of the anion on diffusivity and mobility of ionic liquids composite polybenzimidazol membranes”. *Electrochimica Acta*, v. 354, pp. 136666.
- Dang, D., Zeng, R., Chen, X., Su, X., Yang, X., Su, H., Wu, C., Zhang, L., 2021. “Natural wood derived robust carbon sheets with perpendicular channels as gas diffusion layers in air-breathing proton exchange membrane fuel cells (PEMFCs)”. *Catalysis Communications*, v. 159, pp. 106351.
- Di, Y., Yin, X., 2019. “Reinforced proton conductivity through imidazole-loaded cellulose nanofibers for proton exchange membranes”. *Material Research Express*, v. 6, pp. 116403.
- Fan, L., Tu, Z., Chan, S. H., 2022. “Recent development in design a state-of-art proton exchange membrane fuel cell from stack to system: theory, integration and prospective”. *International Journal of Hydrogen Energy*, p. 1-38.
- Fiuza, R. A., Santos, I. V., Fiuza, R. P., José, N. M., Boaventura, J. S., 2011. “Characterization of electrolyte polyester membranes for application in PEM fuel cells”. *Macromolecular Symposia*, v. 299/300, p. 234-240.
- Giffin, G. A., Pigga, M., Lavina, S., Navarra, M. A., D’Epifanio, A., Scrosati, B., Di Noto, V., 2012. “Characterization of sulfated-zirconia/Nafion® composite membranes for proton exchange membrane fuel cells”. *Journal of Power Sources*, v. 198, p. 66-75.
- Goo, B-H., Paek, S. Y., Munsur, A. Z. al, Choi, O., Kim, Y., Kwon, O. J., Lee, S. Y., Kim, H-J., Kim, T-H., 2022. “Polyamide coated Nafion composite membranes with reduce hydrogen crossover produced via interfacial polymerization”. *International Journal of Hydrogen Energy*, v. 47, p. 1202-1216.
- Gosh, P., Ganguly, S., Kargupta, K., 2022. “Phosphosilicate nano-network (PPSN)-polybenzimidazole (PBI) composite electrolyte membrane for enhanced proton conductivity, durability and power generation of HT-PEMFC”. *International Journal of Hydrogen Energy*, v. 47, p. 32287-32302.

- Gottesfeld, S., Dekel, Dario., Page, M., Bae, C., Yan, Y., Zelenay, P., Kim, Y. S., 2018. "Anion exchange membrane fuel cells: Current status and remaining challenges". *Journal of Power Sources*, v. 31, p. 170-184.
- Gouérec, P., Poletto, L., Denizot, J., Sanchez-Cortezon, E., Miners, J. H., 2004. "The evolution of the performance of alkaline fuel cells with circulating electrolyte". *Journal of Power Sources*, v. 129, p. 193-204.
- Gülzow, E., 1996. "Alkaline Fuel Cells: a critical review". *Journal of Power Sources*, v. 61, p. 99-104.
- Hasani-Sadrabadi, M. M., Dashtimoghadam E., Majedi, F. S., Kabiri, K., Solati-Hashjin, M., Moaddel, H., 2010. "Novel composite proton exchange membranes based on Nafion® and AMPS-modified mntmorillonite for fuel cell applications". *Journal of Membrane Science*, v. 365, p. 286-293.
- Hossen, M. M., Hasan, M. S., Sardar, M. R. I., Haider, J. bin, Mottakin, Tammeveski, K., Atanassov, P., 2023. "State-of-the-art and developmental trends in platinum group metal-free cathode catalyst for anion exchange membrane fuel cell (AEMFC)". *Applied Catalysis B: Environmental*, v. 325, pp. 121733.
- Huang, J., Yu Z., Tang, J., Wang, P., Tan, Q., Wang, J., Lei, X., 2022. "A review on anion exchange membranes for fuel cells: Anion-exchange polyelectrolytes and synthesis strategies". *International Journal of Hydrogen Energy*, v. 47, p. 27800-27820.
- Iulianelli, A., Basile, A., 2012. "Sulfonated PEEK-based polymers in PEMFC and DMFC applications: A review". *International Journal of Hydrogen Energy*, v. 37, p. 15241-15255.
- Jankowska, I. A., Pogorzelec-Glaser, K., Ławniczak, P., Matczak, M., Pankiewicz, R., 2021. "New liquid-free proton conductive nanocomposite based on imidazole-functionalized cellulose nanofibers". *Cellulose*, v. 28, p. 843-854.
- Jin, Y., Wang, T., Che, X., Dong, J., Liu, R., Yang, J., 2022. "New high-performance bulky N-heterocyclic group functionalized poly(terphenyl piperidinium) membranes for HT-PEMFC applications". *Journal of Membrane Science*, v. 641, pp. 119884.
- Kalientkova, V., Mosina, V. C., Paulino, C., 2021. "The Groovy TMEM16 Family: Molecular Mechanisms of Lipid Scrambling and Ion Conduction". *Journal of Molecular Biology*, v. 433, pp. 166941.
- Kang, D. W., Kang, M., Yun, H., Park, H., Hong, C. S., 2021. "Emerging Porous Solid Electrolytes for Hydroxide Ion Transport". *Advanced Functional Materials*, v. 31, pp. 2100083.
- Kumari, M., Sodaye, H. S., Bindal, R. C., 2018. "Cross-linked sulfonated poly(ether ether ketone)-poly ethylene glycol/silica organic-inorganic nanocomposite membrane for fuel cell application". *Journal of Power Sources*, v. 398, p. 137-148.
- Li, C., Yang, Z., Liu, X., Zhang, Y., Dong, J., Zhang, Q., Cheng, H., 2017. "Enhanced performance of sulfonated poly(ether ether ketone) membranes by blending fully aromatic polyamide for practical application in direct methanol fuel cells (DMFCs)". *International Journal of Hydrogen Energy*, v. 42, p. 28567-28577.
- Lim, I. S., Lee, Y. I., Kang, B., Park, J. Y., Kim, M. S., 2022. "Electrochemical performance and water management investigation of polymer electrolyte membrane fuel cell (PEMFC) using gas diffusion layer with polytetrafluoroethylene (PTFE) content gradients in through-plane direction". *Electrochimica Acta*, v. 421, pp. 140509.
- Liu, C., Li, X., Zhang, S., Li, Z., Cao, Y., Jian, X., 2014. "Synthesis and characterization of sulfonated polybenzimidazoles containing 4-phenyl phthalazinone groups for proton exchange membrane". *Solid State Ionics*, v. 261, p. 67-73.
- Liu, Q., Wang, X., Zhang, X., Ling, Z., Wu, W., Fu, X., Zhang, R., Hu, S., Li, X., Zhao, F., Bao, X., 2022. "Polyethyleneimine-filled sepiolite nanorods-embedded poly (2,5-benzimidazole) composite membranes for wide-temperature PEMFCs". *Journal of Cleaner Production*, v. 359, pp. 131977.
- Long, C., Wang, Z., Zhu, H., 2021. "High chemical stability anion exchange membrane based on poly(aryl piperidinium): Effect of monomer configuration on membrane properties". *International Journal of Hydrogen Energy*, v. 46, p. 18524-18533.
- Lou, L. and Pu, H., 2011. "Preparation and properties of proton exchange membranes based on Nafion® and phosphonic acid-functionalized hollow silica spheres". *International Journal of Hydrogen Energy*, v. 36, p. 3123-3130.
- Masnadi, S. M., Grace, J. R., Bi, X. T., Lim, C. J., Ellis, N., 2015. "From fossil fuels towards renewables: inhibitory and catalytic effects on carbon thermochemical conversion during co-gasification of biomass with fossil fuels". *Applied Energy*, v. 140, p. 196-209.
- McLean, G. F., Niet, T., Prince-Richard, S., Djilali, N., 2002. "An assessment of alkaline fuel cell technology". *International Journal of Hydrogen Energy*, v. 27, p. 507-526.
- Merle, G., Wessling, M., Nijmeijer, K., 2011. "Anion exchange membranes for alkaline fuel cells: a review". *Journal of Membrane Science*, v. 377, p. 1-35.
- Miyaniishi, S., and Yamaguchi, T., 2016. "Ether cleavage-triggered degradation of benzyl alkylammonium cations for polyethersulfone anion exchange membranes". *Physical Chemistry Chemical Physics*, v. 17.
- Mustain, W.E., Chatenet, M., Page, M., Kim, Y. S., 2020. "Durability challenges of anion exchange membrane fuel cells". *Journal of Energy and Environmental Science*, v. 13, p. 2805-2838.

- Oh, B. H., Kim, A. R., Yoo, D. J., 2019. "Profile of extended chemical stability and mechanical integrity and high hydroxide ion conductivity of poly(ether imide) based membranes for anion exchange membrane fuel cells". *International Journal of Hydrogen Energy*, v. 44, p. 4281-4292.
- Pinar, F. J., Cañizares, P., Rodrigo, M. A., Ubeda, B., Lobato, J., 2012. "Titanium composite PBI-based membranes for high temperature polymer electrolyte membrane fuel cells. Effect on titanium dioxide amount". *RSC Advances*, v. 2, p. 1547-1556.
- Proch, S., Stenström, M., Eriksson, L., Andersson, J., Sjöblom, G., Jansson, A., Westlinder, J., 2020. "Coated stainless steel as bipolar plate material for anion exchange membrane fuel cells (AEMFCs)". *International Journal of Hydrogen Energy*, v. 45, p. 1313-1324.
- Prykhodko, Y., Fatyeyeva, K., Hespel, L., Marais, S., 2021. "Progress in hybrid composite Nafior®-based membranes for proton exchange fuel cell application". *Chemical Engineering Journal*, v. 409, pp. 127329.
- Rao, S. S., Hande, V. R., Sawant, S. M., Praveen, S., Rath, S. K., Sudarshan, K., Ratna, D., Patri, M., 2019. "α-ZrP nanoreinforcement overcomes the trade-off between phosphoric acid durability and thermomechanical properties: nanocomposite HTPEM with stable fuel cell performance". *ACS Applied Materials & Interfaces*, v. 11, p. 37013-37025.
- Realpe, A., Romero, K. A., Acevedo, M. T., 2015. (In Spanish) "Síntesis de membranas de intercambio protónico a partir de mezcla de poliéster insaturado y látex natural, para su uso en celdas de combustible". *Información Tecnológica*, v. 26, p. 55-62.
- Rosenberg, E., Lind, A., Espersen, K. A., 2023. "The impact of future energy demand on renewable energy production - case of Norway". *Energy*, v. 61, p. 419-431.
- Roy, T., Wanchoo, S. K., Pal, K., 2021. "Synergetic proton-conducting effect of sulfonated PEEK-MO<sub>2</sub>-CNT membranes for PEMFC applications". *Ionics*, v. 27, p. 4859-4873.
- Shen, X., Liang, X., Xu, Y., Yu, W., Li, Q., Ge, X., Wu, L., Xu, T., 2023. "In-situ growth of PPy/MnO<sub>x</sub> radical quenching layer for durability enhancement of proton exchange membrane in PEMFCs". *Journal of Membrane Science*, v. 675, pp. 121556.
- Speirs, J., Mcglade, C., Slade, R., 2015. "Uncertainty in the availability of natural resources: fossil fuels, critical metals and biomass". *Energy Policy*, v. 87, p. 654-664.
- Sun, Y., Lv, H., Zhou, W., Zhang, C., 2020. "Research on hydrogen permeability of polyamide 6 as the liner material for type IV hydrogen storage tank". *International Journal of Hydrogen Energy*, v. 45, p. 24980-24990.
- UN, 2022, World Population Reaches 8 Billion of People (in Portuguese), Organização das Nações Unidas, População Mundial Atinge 8 Bilhões de Pessoas, Nova Iorque, <https://news.un.org/pt/story/2022/11/1805342>. Accessed 15 March 2023.
- Wang, C., Shen, B., Xu, C., Zhao, X., Li, J., 2015. "Side-chain-type poly(arylene ether sulfone)s containing multiple quaternary ammonium groups as anion exchange membranes" *Journal of Membrane Science*, v. 492, pp. 281-288.
- Wu, S. and Chiou, A. H. 2021. "The study on a new method of preparing PMMA forming composite bipolar plate". *Scientific Reports*, v. 11, pp. 8753.
- Xu, P. Y., Zhou, K., Han, G. L., Zhang, Q. G., Zhu, A. M., Liu, Q. L., 2014. "Fluorene-containing poly(arylene ether sulfone)s as anion exchange membranes for alkaline fuel cells". *Journal of Membrane Science*, v. 457, pp. 29-38.
- Xue, J., Liu, X., Zhang, J., Yin Y., Guiver, M. D., 2020. "Poly(phenylene oxide)s incorporating N-spirocyclic quaternary ammonium cation/cation strings for anion exchange membranes" *Journal of Membrane Science*, v. 595, pp. 117507.
- Ye, G., Li, K., Xiao, C., Chen, W., Zhang, H., Pan, M., 2010. "Nafion®-titania nanocomposite proton exchange membranes". *Journal of Applied Polymer Science*, v. 120, p. 1186-1192.
- You, W., Noonan, K. J. T., Coates, G. W., 2020. "Alkaline-stable anion exchange membranes: A review of synthetic approaches". *Progress in Polymer Science*, v. 100, pp. 101177.
- Zhang, Z., Xiao, X., Yan, X., Liang, X., Wu, L., 2019, "Highly conductive anion exchange membranes based on one-step benzoylation modification of poly(ether ether ketone)". *Journal of Membrane Science*, v. 574, p. 205-211.
- Zheng, Y., Omasta, T. J., Peng, X., Wang, L., Varcoe, J. R., Pivovar, B. S., Mustain, W. E., 2019. "Quantifying and elucidating the effect of CO<sub>2</sub> on the thermodynamics, kinetics and charge transport of AEMFCs". *Journal of Energy and Environmental Science*, v. 12, p. 2806-2819.
- Zhu, L. Y., Li, Y. C., Liu, J., He, J., Wang, L. Y., Lei, J. D., 2022. "Recent developments in high-performance Nafion membranes for hydrogen fuel cells applications". *Petroleum Science*, v. 19, p. 1371-1381.

## 9. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.