Review Paper

Production of Green Hydrogen Employing Proton Exchange Membrane Water Electrolyzer: Characterization of Electrolyte Membrane. A Critical Review

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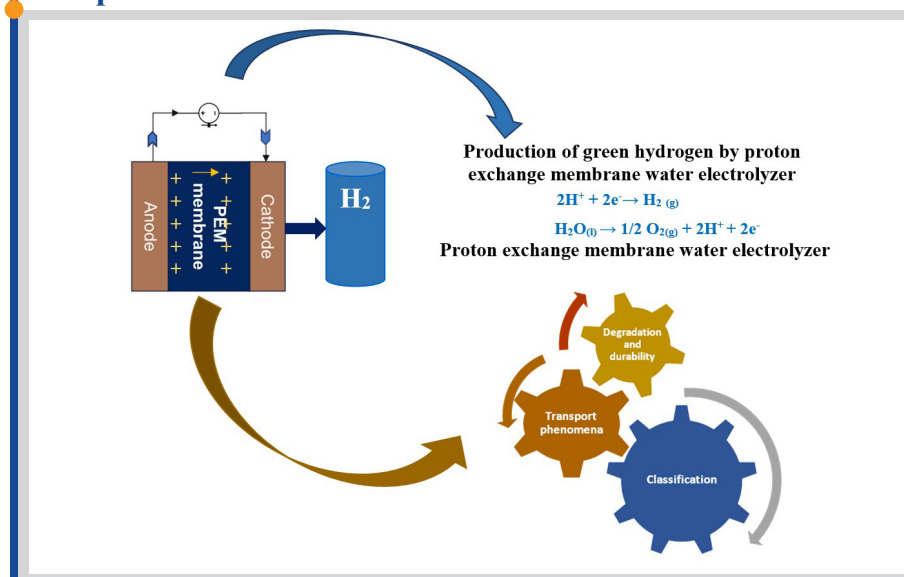
Article info

Keywords

Highlights

- Green hydrogen is essential for the development and success of renewable energy, the energy transition, and the reduction of greenhouse gas emissions.
- The development of proton exchange membrane water electrolyzer technology will accelerate the production and use of green hydrogen.
- This review offers a complete description of the solid electrolyte which is in the form of a membrane.

Graphical abstract

Abstract

In the framework of developing renewable energies and reducing greenhouse gas emissions, green hydrogen has become a crucial factor in the energy revolution. This energy vector can be manufactured from biomass, biogas reforming, or by splitting water, which is one of the most abundant and limitless power generators on earth. Proton exchange membrane water electrolysis (PEMWE) has gained considerable attention as an energy conversion system for hydrogen production. It is considered the preferred choice for green hydrogen production owing to its energy efficiency, low capital cost, flexibility, safety, and durability. The membrane is the beating heart of the PEMWE electrolysis cell. The most used PEM membrane is perfluorosulfonic acid (PFSA) membranes, especially Nafion. However, these membranes have weaknesses that affect production efficiency. Therefore, developing membranes is crucial to improve and enhance the working temperature, optimize mass transportation, avoid catalyst corrosion and electrode flooding, boost effectiveness, and minimize the system's price and complexity. To design high-temperature functioning membranes, modifications to conventional ones include adding various hygroscopic inorganic particles or creating original polymer systems. This work begins with generalities about green hydrogen production using PEMWE. In this section, we will describe the functioning and diverse cell operating parameters, followed by the role and functioning of different components. In the second part, we provide a comprehensive description of the PEMWE membrane, including detailed statements on classification, essential transport phenomena, and the degradation and durability of this electrolyte. Finally, we will conclude with a comparison between commercial membranes and those under development.

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Contents

1. Introduction

The process of climate change known as "global warming" is defined by an overall rise in average temperatures, something that durably alters meteorological balances and ecosystems. The main cause of this phenomenon is the industrial revolution. We have developed, all over the planet, machines, and technologies that consume a lot of energy to operate, using wood, coal, oil, and gas. By burning all these resources to produce energy, greenhouse gases are being released into the atmosphere at an increasing rate, day by day. Hence, we have disrupted the normal balance of the planet. As a result, the climate is warming up.

Hydrogen or green gas is a new perspective, which will revolutionize the future of the energy sector, not only in terms of electricity storage but also in industrial terms.

As an abundant element, hydrogen is essentially found in many natural substances such as fresh water, sea water, biomass... Unfortunately, it is not present in its purest form (H_2 molecule), and as a result, is unable to be utilized directly. Its recovery requires production processes and the metamorphosis of raw materials. The three main production processes are biomass, biogas, and water molecule dissociation including electrolysis using renewable energy sources without greenhouse gas emissions. First, H_2 production from biomass uses organic materials such as crop residues, agricultural waste, food waste, paper waste, wood waste, green waste, and other organic matter. Manufacturing can be achieved through several pathways, including gasification, fermentation, pyrolysis, and biological electrolysis. This type of production from biomass offers sustainability advantages and greenhouse gas emission reductions compared to methods from fossil fuels. However, there are technical and economic challenges to overcome for this method to be widely used on a large scale. [1–5]

Second, the process of manufacturing H_2 from biogas involves two main steps: first, biogas is resulting from the anaerobic fermentation of organic material, microorganisms break down organic matter and produce biogas, which consists predominantly of carbon dioxide (CO_2) and methane (CH_4). After that, the methane in biogas is separated from CO_2 and is then converted to hydrogen using steam reforming. However, the production of hydrogen from biogas can be expensive and requires capital investment. [5–7]

With the methodology of H_2O dissociation, H_2 can be created from one of the most plentiful and limitless basic elements on the planet: water. The hydrogen created will be the cleanest energy carrier that can be produced and used by humanity when the necessary energy input is supplied from renewable energy sources. This process of dissociation of water involves the breaking of O-H bonds, but these bonds are the most energetic ones due to the great difference in electronegativity between oxygen and hydrogen. Nevertheless, many ways are possible to break down the water molecule. These can be grouped into two families; direct thermolysis which is based on the one-step thermal dissociation of water. [8] Although the thermolysis of water is conceptually simple, it is one of the most complicated processes in terms of industrial realization, due to the difficulties in separating hydrogen and oxygen to avoid explosions, a high-temperature heat source exceeding 2500 K must be used to produce a reasonable level of dissociation. The second thermal way of manufacturing H_2 is through multi-step thermochemical cycles that have been proposed and developed as a repetitive set of interactions in which H_2O is decomposed at temperatures below 2000°C [8–11].

The final process of manufacturing is electrolysis, which converts water (H_2O) into hydrogen (H_2) and oxygen (O_2) gases using electricity generated by environmentally friendly sources like solar or wind energy. This process involves the use of an electrolyzer, which is a mechanism containing two electrodes separated by a water-permeable membrane. There are several types, including alkaline electrolysis, in which an alkaline solution of potassium or sodium hydroxide is used as the electrolyte. Polymer electrolyte membrane (PEM) electrolysis uses a solid polymer electrolyte membrane that allows only positively charged protons to pass through it [12]. The electrodes are typically made of platinum or other noble metals. Solid oxide electrolysis (SOE) uses a solid oxide electrolyte typically made of ceramic materials. It operates at high temperatures (800-1000°C) and produces both hydrogen and carbon monoxide, which is a raw substance that can be used to synthesize other chemicals. Finally, photoelectrochemical (PEC) is the new generation. In PEC water splitting, a semiconductor material is used as the electrode, which absorbs light energy and converts it into electrical energy to drive the water-splitting reaction [13–18].

Each type of water electrolysis is distinguished by both positive and negative aspects depending on the specific application and requirements. However, at the theoretical level, several studies indicate that Proton Exchange Membrane Water Electrolyzers (PEMWEs) is the most efficient option for renewable hydrogen manufacturing [12–14]. This is due to their high energy efficiency, fast response to electrical load changes, safety, and low carbon emissions. PEM electrolyzers typically have an energy efficiency

ranging from 70% to 80%, allowing them to produce H_2 using less electrical energy than other types of electrolyzers [12]. Even at the experimental level, this type of electrolyzer is often recommended for manufacturing at the laboratory level due to its energy efficiency and safety. Additionally, PEM electrolyzers do not produce dangerous oxygen or explosive gases, which makes them safer to use, they also have a relatively small footprint and can be easily integrated into existing laboratory facilities. They are also lightweight and portable, making it easy to move to different parts of the laboratory as needed. Finally, PEMWEs can produce hydrogen on demand, which is particularly useful for laboratory applications where precise amounts of hydrogen are needed. By combining these advantages, it is clear that PEM electrolyzers are a very interesting option for hydrogen production at the laboratory level [19–23].

The development and optimization of PEMWE is a highly active research area, with significant advancements in materials, design, and system integration in recent years. However, there are still several research gaps and challenges to increase the effectiveness, durability, and scalability of PEMWE. Characterization of the electrolyte membrane is a major research field that requires further attention [24, 25].

The electrolyte membrane plays a critical and crucial role, the characteristics such as proton conductivity, chemical stability, mechanical strength, and water uptake, can have an important effect on the PEMWE's potency and robustness. Despite the importance of the electrolyte membrane, there are still several research gaps in the characterization and optimization of this component. For example, it´s important to clearly understand the origins of deterioration and performance limitations of different types of electrolyte membranes under different operational circumstances, including high current densities and high temperatures [24, 25]. In the interests of improving the functionality and longevity of electrolyte membranes, new types of polymers must also be provided, and design approaches should be updated to modify the membrane's physical properties.

Therefore, a critical review of the description of electrolyte membranes would provide a comprehensive analysis of the current state-of-the-art and identify the key research gaps in this domain to inform future research directions and guide the development. This essay aims to discuss and examine the functioning of PEMWE to produce green hydrogen. More specifically, in the first part, this review will provide a general idea about the functioning, components, thermodynamic and electrochemical aspects of the electrolytic cell. Subsequently, we will focus on the crucial component of the electrolytic cell, which is the solid electrolyte. We will start by classifying the different types of membranes and discussing the essential transport phenomena, degradation, and durability. After that, we will propose a series of current and future challenges tentatively.

2. Production of green hydrogen

Since its inception, the transition to green hydrogen has been challenging due to the absence of molecular hydrogen in the natural environment. Instead, it must be produced by dissociating the H_2O water molecule. Currently, the main technique used to generate hydrogen is the steam reforming of natural gas or other fossil fuels. The critical and major inconvenience of this process is the generation of carbonic gases, such as carbon monoxide, that have a high carbon content. Yet, the electrochemical decomposition of the molecule of water into hydrogen and oxygen provides high-quality hydrogen. Electrolyzers using proton exchange membranes (PEMs) have considerable potential for the generation of hydrogen, they are compact, electrically efficient, produce very pure hydrogen (with little to no pollution from the electrolyte), require little maintenance, and can be fueled by electricity generated from sources of clean energy. Water electrolysis is the subject of scientific study in the context of the development of green hydrogen. General Electric (GE) adopted a solid polymer electrolyte concept to develop the first water electrolyzer [26]. Grubb later employed a solid sulfonated polystyrene membrane as the electrolyte [26]. The fact that an acidic solid is utilized as an electrolyte instead of a liquid gave rise to the name (PEM) for this novel technology. The operating temperature is around 50-80°C for pressures of 10 to 200 bar, and its efficiency reaches 85% [12, 27, 28]. Unfortunately, there hasn't been enough study on PEM electrolysis during the previous century, and therefore, there are still many problems and challenges to overcome.

2.1. Component and general operating principle of PEMWE

A variety of components constitute an electrolysis cell, and they all work together to ensure that the oxidation-reduction reaction that electrolysis uses to create hydrogen and oxygen proceeds as intended. The polymer electrolyte configuration is the crucial element of the system, as it represents the main site of hydrogen production. The essential components of this assembly are illustrated in Fig. 1.

PEM membrane: a proton exchange membrane separates the anode and cathode, the electrolyte is an ion exchange membrane of the Nafion® type, a polymer created in the 1950s. This electrolyzer named PEMWE is distinguished by the fact that it uses an extremely thin (20-300 micrometers), gas-tight, and strongly acidic polymer membrane as an electrolyte, which contains sulfonic functional groups ($R-SO_3H$) that are responsible for the ion exchange mechanism. In the second part, we will discuss this membrane in more detail [29–31].

Electrodes: A PEMWE cell has two electrodes: an anode and a cathode. These electrodes must be porous while maintaining sufficient electronic conductivity to ensure proper electronic transfers. Each electrode is the site of an electrochemical reaction and is directly connected to a current collector. Because the reactions that take place are different, the materials that make up the electrodes are also different. The electrodes consist of a layer of catalytic material (catalysts + ionomer) and a diffusion layer [32–34].

Transport diffusion layers: They are in the form of an additional porous layer that is placed against each of the electrodes with a thickness of 100 to 300 µm. Specifically, carbon fiber is used at the cathode and a titanium disc at the anode [32–34]. In addition to eliminating the oxygen generated by the reaction, they assist in transferring the reactant H_2O by capillary action from the bipolar plates to the catalytic zone. However, the PEM electrolyzer system can function inadequately due to incorrect oxygen evacuation and concentration in the PTL and the pores of the catalytic layer [28, 35]. Such an accumulation of oxygen can damage the water transport across the PTL, resulting in the dehydration of the polymer and affecting the Oxygen Evolution Process (OER). It should be noted that water also removes excess heat within the electrolyzer. Along with the described mass transfer, the porous transport layer should ensure that the catalytic layer and the bipolar plate have sufficient electrical contact for the electrons to migrate to the cathode, where protons interact to produce H_2[28, 34–37]. The role of transport diffusion layers is twofold: to ensure good electronic conduction between the bipolar plates and the catalytic layer, and to allow a correct supply of water while allowing the dioxygen and dihydrogen bubbles to be evacuated. Typically, carbon is used for the cathode section as a diffusion layer and titanium for the negative side.

There are two types of plates [38]: sintered PTLs, which are in the form of a porous layer obtained by thermal sintering of titanium beads, and regular PTLs, which are titanium grids covered with a microporous layer to facilitate the transport of material. Sintered PTLs have three sub-categories according to the shape of the particles used: irregular particles, spherical particles, and titanium fibers. The diameter of the pores varies between 10 µm and 100 µm and their porosity is between 20% and 60% [38–40]. The diameter of the pores for regular PTLs is greater than approximately 150 µm. The advantage of regular PTLs is their low cost compared to those made by sintering. Nevertheless, they risk degrading the catalytic layer due to thick fibers and increasing the ohmic resistance due to large pores [38–42].

Bipolar plates: are expensive components, contributing around 48% of the overall cost of a PEMWE [43]. They have a dual function of supplying current and ensuring the evacuation of produced gases, as well as transporting water. At the heart of an electrolysis stack, they ensure the mechanical strength of the stack while isolating the cells from each other to avoid mixing the produced reactants and acting as excellent conductors of heat and electrons. The choice of materials is delicate due to the challenging conditions to which these plates are exposed (high potential and acidic environment). Currently, metals such as stainless steel, titanium, graphite, coated stainless steel, copper plates, and other nitride-based alloys are used to make these plates, but none of these materials are inexpensive and all suffer from several operational problems [43–45]. Excellent electrical conductivity, resistance to corrosion, great mechanical strength, and low weight are all characteristics of titanium. However, it is an expensive material, difficult to machine, and characterized by the formation of a surface oxide layer [46], which decreases cell performance over time after prolonged use and adversely affects its electrical and thermal conductivity. When hydrogen is produced, titanium bipolar plates on the cathode side can become hydrogen embrittled, causing the formation of hydrides (T_iH_2) on the plate surface [46–48]. This occurs when the titanium material's solubility limit for hydrogen is surpassed (a few hundred ppm), increasing the risk of stress cracking [46]. Titanium becomes prone to corrosion when subjected to hydrogen gas at extreme heat (>80°C)

attributable to the apparition of hydrides in the crystal structure. Additionally, the high-pressure hydrogen resulting from the reduction activities facilitates hydrogen absorption in the metal bipolar plates [49]. To limit this damage, the separator plates can be coated with gold or platinum, guaranteeing their durability and limiting oxidation by avoiding the formation of the oxide layer; however, this increases the cost [47]. In contrast, graphite has been explored due to its high conductivity, but its usage is hindered by its low mechanical strength, high rate of corrosion, manufacturing difficulties, and extremely high cost. Due to its low mechanical strength, a thicker material is required, which raises ohmic resistance. Furthermore, due to the high rates of corrosion, current collectors are not in good contact with them. The high cost of titanium and graphite motivates research and development of less expensive base metals. These alternative base metals are often coated to shield them from harsh conditions in an electrolysis cell. Stainless steel is among the most economical choices, but it also has some disadvantages. Due to the corrosive acidic atmosphere, it corrodes extremely quickly, requiring a coating to maintain tolerable longevity. Nevertheless, it is challenging to apply a coating that satisfies the requirements of this environment since doing so typically increases ohmic resistance, and tiny coating flaws can degrade the underlying metal, preventing corrosion protection [43–49]. The morphology of the bipolar plates is critical in defining the performance of an electrochemical cell. These distributors can consist of channels machined into the bipolar plates, ensuring a uniform distribution of the reagents on the electrodes, and guaranteeing optimal use of their active surface. Different geometries of fluid circulation channels can be defined [47–49].
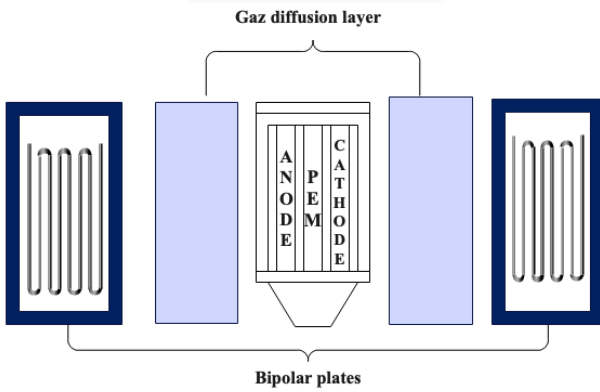

Fig. 1. Component of a PEMWE system. Source: Authors

The general operating principle of PEMWE (Fig. 2) can be described in the following steps: first, demineralized water, there is no electrolytic additive is fed into the electrolyzer unit, then when a sufficiently high electrical potential is applied across the anode and cathode, an electric field is generated across the PEM [12]. The splitting of the water molecules into hydrogen and oxygen ions is catalyzed by this electric field. The hydrogen ions (protons H^+) are then clearly directed via the PEM to the cathode, while the oxygen ions combine to generate oxygen gas at the anode. Protons are selectively permitted to pass through the PEM to the cathode while hydroxide ions are inhibited. The following equation indicates that on the positive side, protons combine with electrons from the external circuit to generate hydrogen gas. [13, 28]:

At the cathode: $2H^+ + 2e^- \rightarrow H_{2(g)}$ (1)

At the anode: $H_2O_{(l)} \rightarrow 1/2\ O_{2(g)} + 2H^+ + 2e^-$ (2)
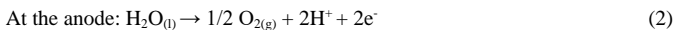
Hydrogen gas is captured and kept in storage for usage in a variety of industrial and fuel cell activities, among other things.

The PEMWE system's overall performance is influenced by several factors, including the voltage and current applied, the quality of the water used, the temperature and pressure of the system, and the design of the electrolyzer unit. Higher voltage and current will generally result in higher hydrogen production rates, but also higher energy consumption. The quality of the water used can also impact the system efficiency, as impurities in the water can lead to electrode degradation and reduced system performance.
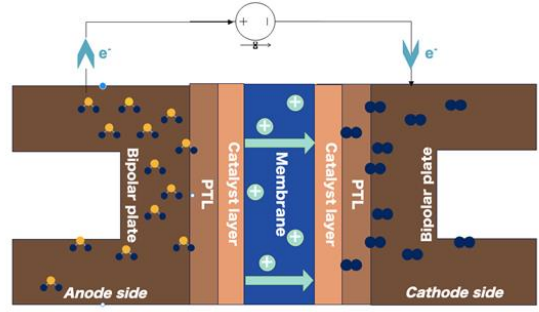

Fig. 2. Operating principle of a PEMWE cell. Source: Authors

2.2. Thermodynamic aspects

In the case of PEMWE, the thermodynamic analysis helps to understand the energy requirements and efficiencies of the hydrogen production process. From a thermodynamic perspective, the dissociation of the water molecule while electrolysis is an endothermic, not a spontaneous, reaction, it is then necessary to bring energy to realize it. According to the first principle, the Gibbs-Helmholtz equation represents the enthalpy of the reaction and the minimal energy required for dissociation:

$$\Delta r(T,P) = \Delta rG(T,P) + T\Delta rS(T,P)$$ (3)
$$= Welec + Q$$

- Enthalpy variation $\Delta(T,P)$: the total energy needed to initiate the electrolysis process.
- Gibbs free energy variation $\Delta(T,P)$: the level of electrical energy required for the water dissociation.
- Variation of entropy $T\Delta(T,P)$: the quantity of thermal energy required to separate the molecule of water.

The operational temperature and pressure impact these values.
At standard conditions,$T° = 298\ K$ and $P° = 1\ bar$: [50–57]
$\Delta rH°= 285.840\ kJmol^{-1}$
$\Delta rS° = 0.16315\ kJmol^{-1}K^{-1}$
$\Delta rG°= 237.22\ kJmol^{-1}$

- The quantity of electrical energy necessary for the electrolysis of water procedure is used to determine the reversible voltage $E_{rev}[V]$, which represents the theoretical voltage required to be delivered between the two electrodes to generate the activity of dissociation : [50–57]

$$E_{rev} = \frac{\Delta rG}{nF}$$ (4)

with

F Faraday constant (= 96 485 $Cmol^{-1}$)
quantity of electrons that were transferred during the reaction. For water electrolyzer $n = 2$.

- Thus, the enthalpy variation ΔrH allows us to define the thermoneutral voltage $Ethe[V]$which corresponds to the isothermal operation of the electrolyzes: [53–56]

$$E_{thr} = \frac{\Delta rH}{nF}$$ (5)

- The thermo-neutral voltage refers to the electrical voltage that must be applied to the electrolytic device to make the electrolysis reaction possible from a thermodynamic perspective, the potential E_{ther} is applied to carry out the electrolysis under the adiabatic conditions. In other words,$_{the}$ is the intensity that conforms to be applied to the cell for it to generate the reaction's necessary heat ether. Under standard conditions $T° = 298\ K$ and $P° = 1\ bar$, these two voltages are worth:

$$E°_{rev} \approx 1,23\ V, \quad E°_{ther} \approx 1,48\ V$$

An additional voltage corresponding to TΔrS/2F (0.25 V) should be applied in addition to the thermodynamic potential to ensure the decomposition reaction of the molecule water [51].

The practical or real tension of the V_{real} system is considered as the sum of the reversible of the E_{rev} cell, the voltage drops R*I through the ohmic

resistance, and the activation and concentration surges at the level of the positives and negatives electrodes. The voltage is then calculated according to the following relation: [53–57]

$$V_{real} = E_{rev} + \eta_{act} + \eta_{conc} + \eta_{ohm} \tag{6}$$

with:

E_{rev}: reversible voltage (V)
η_{act}: activation overvoltage (V)
η_{conc}: mass transport overvoltage (V)
η_{ohm}: ohmic overvoltage (V)

Once an electrical charge is applied to a PEMWE cell, the voltage at its terminals V_{real} is defined as a function of Erev. However, in practice, the operation of an electrolyzer is subject to certain losses which will contribute to the increase of the cell voltage, they are classified into three groups according to their origin: activation overvoltages, ohmic overvoltages, and material transport or concentration overvoltages [50–57].

The activation overvoltage: the beginning and the execution of an electrolytic process at the surface of each electrode requires and requires the crossing of an energetic barrier called activation energy, which ensures the transfer of charge to the electrodes.

The distribution and application of the catalyst, its structure, the structure of the electrode, the functioning heat, and the positioning of the active reaction site are all physical and chemical properties that influence the power losses. [50–58]

The difference between the two sides provides the activation overvoltage of the cell according to the following reaction:

$$\eta_{act} = \eta_{act}{}^a - \eta_{act}{}^c \tag{7}$$

The anode activation overvoltage is higher than the cathode overvoltage since the kinetics of water oxidation (oxygen production) is much faster than hydrogen reduction. The anode activation overvoltage is counted positively ($\eta_{act}a \geq 0$) while the cathode activation overvoltage is counted negatively ($_tc \leq 0$).

Since OER is a much slower and more complex reaction than HER, the total activation overvoltage will be mainly controlled by the activation overvoltage due to OER [55–56].

$$\eta^a = \frac{RT}{\alpha_a nF} \ln(\frac{i}{i_{a,0}}), \eta^c = \frac{RT}{\alpha_c nF} \ln(\frac{i}{i_{c,0}}) \tag{8}$$

Mass transport/concentration overvoltage: considering that the Water's dissociation mechanism to produce hydrogen occurs exclusively at the membrane-electrode boundary, the porous electrode serves as the conduit via which all mass flows: first, H_2O is transferred to the catalyst layer by flow channels crossing PTLs, second, the produced reactants which are hydrogen and oxygen are then transferred to the outlet through the flow channels.

However, these losses evolve by the accumulation of gases on the active layers and/or by limiting water circulation in the diffusion layers. The formation of bubbles of dihydrogen and dioxygen during water electrolysis also contributes to the increase in material transport losses [55–59]. Using the Nernst equation, these parameters at the two electrodes could be determined as follows: [58]

$$\eta_{conc} = \frac{RT_a}{4F} \ln(\frac{C_{O_2,m}}{C_{O_2,m_0}}) + \frac{RT_c}{2F} \ln(\frac{C_{H_2,m}}{C_{H_2,m_0}}) \tag{9}$$

where $CO_2,0$ and $CH_2,m0$ indicate the concentrations of the reactants O_2 et H_2, respectively, at the MEA interface according to the working conditions.

Ohmic overvoltage: the ohmic overvoltage is a result of ohmic losses that occur inside the cell, including electrical losses brought on by the resistance of different components. Nevertheless, at the membrane level, ionic losses are the predominant ohmic losses [58].

Ohm's law is maintained by the ohmic surge, which is directly correlated with the applied current I, which can be determined by the equation shown below:

$$\eta_{ohm} = R * I \tag{10}$$

As a result of the different voltages explained above, there are three types of operation:

- $V_{real} = E_{the}$: no heat exchange with the environment, i.e., the necessary heat is contributed by the internal irreversibility of the reaction.
- Erev < V_{real}<E_{the}: need to use an external heat source because the

irreversibility does not compensate for the heat needed to dissociate the water.

- V_{real}>E_{ther}: the electrolyze must be cooled because there is excess heat due to the reaction.

In conclusion, the thermodynamic aspects of PEMWE have an important function in understanding the energy requirements and efficiencies of the H_2 production process. The thermodynamic analysis helps to determine the minimum voltage required to drive the PEMWE process, as well as the maximum thermodynamic efficiency that can be achieved. The actual voltage required and the efficiency of PEMWE depend on various factors such as electrode overpotentials, membrane resistance, temperature, and pressure.

2.3. PEM water electrolyzer performance

The h yield is a technical parameter that is usually specified with values between 0 and 1 or 0% and 100%. The electrolyzer is a process that is based on an electric current, it is then characterized by energy efficiency, and electricity is faradic [54–59].

- Energy efficiency

The h energy efficiency is characterized as the percentage of the voltage E_{ther} and the amount of real energy needed V_{real}. In this case, the yield is calculated in relation to the change in enthalpy ΔrH associated with Ether:

$$h_{ener} = \frac{E_{ther}}{V_{real}} \tag{11}$$

- Electrical Efficiency

Electrical efficiency is associated with E_{rev}, it is calculated by:

$$h_{elec} = \frac{E_{rev}}{V_{real}} \tag{12}$$

According to the following equation, this electrical efficiency can be evaluated as the proportion of chemical energy produced W_{H2} to electrical energy needed W_{el}: [54, 58]

$$h_{elec} = \frac{W_{H_2}}{W_{elec}} = \frac{N_{\dot{H}_2} H_v}{v_{real} * i * t} \tag{13}$$

where NH is the molar amount of H_2 generated, H_V is the heat, and V_{real} represents the cellular potential.

- Faradic efficiency

This ρ yield relates the theoretical quantity of reagents and the quantity of gas produced by the electrolyzer. It can then be expressed for hydrogen and oxygen according to the following reaction: [54–58]

$$h_{F_{H_2}} = \frac{2FN_{H_2}}{i}, h_{F_{O_2}} = \frac{4FN_{\dot{O}_2}}{i} \tag{14}$$

where NH·$_2$ and NO·$_2$[mol/s]: the molar flows of hydrogen and oxygen produced by the electrolyzer.

The total faradic yield is then defined by multiplying the two yields:

$$h_T=h_{FH}*h_{FO} \tag{15}$$

2.4. Electrochemical aspects

The theoretical thermodynamic potentials of the two catalytic electrodes (anode\cathode) are determined by the Nernst relation according to the chemical compounds involved in the two half-equations (1,2). The water oxidation reaction happens under the effect of the electric field. After traversing the membrane, the protons are transformed at the cathode to form dihydrogen [56–59]

At the anode

$$E_{(O_2/H_2)} = E^{\circ}{}_{(O_2/H_2o)} + \frac{RT}{nF} \ln(\frac{(a_{H^+})^4 (a_{O_2})}{(a_{H_2O})^2}) \tag{16}$$

At the cathode

$$E_{(H^+/H_2)} = E^{\circ}{}_{(H^+/H_2)} + \frac{RT}{nF} \ln(\frac{(a_{H^+})^4}{(a_{H_2})^2}) \tag{17}$$

with:

R: the perfect gas constant (8,314 J mol^{-1} K^{-1}).

T: temperature in K.

F: Faraday constant (96 485 C mol^{-1}),

a_x: the activity of chemical species x, for liquid phase water, the activity aH_2O is 1.

For gases, the activity is determined from the partial pressure P_x and the total standard pressure P_0.

$a_x = P_x/P_0$

n: the number of electrons implicated in the half-oxidation\reduction reactions.

2.5. Main advantages and disadvantages of PEM water electrolyzer

Polymer electrolyte membrane water electrolyzer (PEMWE) has numerous benefits over other water electrolysis systems. The use of a polymer membrane as an electrolyte provides several advantages over other types of electrolytes. One of the primary advantages is the process of managing pure hydrogen, which is essential for many industrial and scientific applications. The membrane-electrode assemblies are thin, flexible, and easy to handle, which makes the system more compact and easier to install. Furthermore, the system can operate at high pressure without the need for a hydrogen compressor, reducing the system's expense and complexity. This is because the use of a solid electrolyte permits pressure changes between the anode and cathode without affecting the system's functionality [12, 26, 58].

In addition to the benefits mentioned above, PEMWE can also operate at very high current levels (in the range of several A/cm^2) with excellent energy yields. The ionic charge carriers remain confined within the membrane, which prevents contamination of the products and maximizes the efficiency of the system. PEMWE also allows for high-pressure operation without the need for a hydrogen compressor. This reduces the complexity of the system and makes it easier to operate and maintain. The high-pressure operation of PEMWE is particularly advantageous for laboratory-scale experiments that require precise pressure control. Another advantage of PEMWE for laboratory-scale applications is the ability to operate at very high current levels with excellent energy yields. This allows laboratory researchers to carry out experiments that require high levels of energy input without compromising the system's efficiency or performance [12, 26–30, 58].

So far, despite all PEMWE's benefits, one of the major weaknesses is its high cost. The materials used as catalysts, as well as those used in the bipolar plates and current collectors, must resist the acidic environment caused by using a Nafion membrane. Only noble metals, such as platinum, rhodium, and palladium, which are rare and expensive, can resist these types of conditions. Furthermore, PEMWE requires highly deionized water for the operation to avoid the penetration of metallic impurities via ion-exchange processes. Deionization and purification of water are costly processes, and insufficient water purification may necessitate expensive repair procedures. These factors contribute to the overall cost of the PEMWE system and limit its widespread adoption [12],[26]–[30],[58].

Hydrogen production through (PEMWE) is generally considered a safe and efficient process. However, hydrogen crossover can present a significant challenge in the context of high-performance applications that use thin membranes. Hydrogen crossover occurs when hydrogen gas passes through the membrane into the anode chamber, where it can accumulate in confined spaces and potentially react with oxygen to create an explosive atmosphere [59]. The risk of hydrogen crossover is exacerbated by the properties of hydrogen, which is odorless, colorless, and highly flammable. If left unchecked, hydrogen crossover can compromise the safety and efficiency of the PEMWE process, as well as pose a risk to personnel and equipment. Many safety precautions and measures may be performed to minimize the possibility of hydrogen crossover. For example, gas detectors can be installed to monitor the concentration of hydrogen in the anode chamber, and appropriate pressure control mechanisms can be used to reduce the risk of leaks and explosions. Researchers have also created coverings made of polymers or nanoparticles that can slow down the membrane's absorption of hydrogen. These coatings can be applied to the surface of the membrane or incorporated into the membrane itself, providing an additional layer of protection against hydrogen crossover [60–62].

In conclusion, although the risk of hydrogen crossover cannot be eliminated in PEMWE, appropriate safety measures can significantly reduce the risk and ensure safe and efficient hydrogen production. By implementing these measures, it is possible to minimize the risk of hydrogen crossover and ensure that the production and storage of hydrogen are carried out safely and efficiently.

3. Proton exchange membrane (PEM)

PEMWE and PEMFC (Proton Exchange Membrane Fuel Cell) are both electrochemical devices, PEMFC is a fuel cell that employs hydrogen gas and oxygen obtained from the atmosphere to create electricity, whereas PEMWE is an electrolysis device that uses electrical energy to split water into hydrogen and oxygen gases. Both technologies use a selective membrane (PEM) to facilitate the transfer of protons between the anode and cathode sides of the cell, but there are some key differences between the PEM membrane used in each technology [28, 35–37].

The membrane in the two technologies is typically made from a fluorinated polymer such as Nafion, but for the PEMWE it is typically thicker and more durable than the membrane used in a PEMFC, this is because the water electrolysis process requires a higher voltage than a fuel cell, which can cause more wear and tear on the membrane. A thicker membrane helps to increase durability and prevent degradation over time. Additionally, the membrane used in a must be more durable than the membrane used in a PEMFC, because of the degradation over time due to the harsh chemical conditions, such as the presence of oxygen and chlorine[28, 35–37].

One of the challenges with using a PEM in a fuel cell is preventing the anode and cathode compartments from transferring gas. This happens when hydrogen or other gases permeate from the negative electrode through the membrane to the cathodic sites, which can degrade the cell's efficiency.

The solid electrolyte used in PEM electrolysis is situated at the cell's midsection in the form of a proton exchange membrane. This polymer membrane typically has a thickness that varies between 150-200 μm [63, 64] and is the key component of PEMWE. The membrane plays a crucial role in PEM cells, serving two distinct purposes: ensuring the transfer of H$^+$ and guaranteeing the separation of gases formed on both sides. The properties required for an effective membrane to act as a barrier while allowing the passage of ions include the following [32, 37, 63, 64]:

1. Excellent chemical, mechanical, and electrochemical endurance, as well as robustness under the environmental conditions of the electrolysis system.
2. Strong ionic conductivity and permeability to tolerate voltage levels with minimal resistive losses and eradicate electron transport.
3. Thermal and hydrolytic resistance.
4. Chemical characteristics that satisfy the requirements for the electrode-membrane assembly MEA.
5. Low susceptibility to reactive species to increase effectiveness.
6. High durability and low cost.
7. The capacity of proton exchange membranes to absorb water, which affects both the hydromechanical stability and electrochemical activity is one of the most crucial properties.

The membranes used in the production of electrolysis cells are exclusively perfluorosulfonic acid membranes (PFSA). They are made of a perfluoro sulfonate material containing a hydrophobic polytetrafluoroethylene (PTFE) type backbone and a perfluorinated side chain terminated by a hydrophilic sulphonic SO$_3$H group [65].

Several polymers, such as Fumapem, Flemion, and Aciplex, are used due to their high robustness, high performance, strong oxidative resistance, dimensional stability with temperature fluctuations, strong durability, and high proton conductivity. The side chain length and the space between two of these chains inside the main chain define these materials apart from Nafion® [64].

However, Nafion® membranes (Nafion®115, 117) are currently the popular membranes used in this electrolyzer since they offer many benefits, including the ability to operate at high power density, strong proton transfer, good thermal and mechanical stability, and the potential to perform at a high amperage rate. Nevertheless, to permit the displacement of H$^+$ ions associated with the sulfonate groups, the membrane must continuously be kept saturated with water [32, 37].

Aquivion® membranes from the manufacturer Solvay may also be used. They are also perfluoro sulfonate but have shorter pendant chains than Nafion®. Moreover, they exhibit crystallinity and have a higher glass transition temperature [65].

To limit and reduce the ohmic drop and the size of the system, the membrane must be as thin as possible. However, this membrane is not perfectly impermeable to gases, so some of the reagents produced can pass through it. This phenomenon of membrane permeation to gases can be problematic. Indeed, when the dihydrogen concentration in dioxygen exceeds 4 vol. %, the mixture becomes explosive [62–65]. Therefore, it is necessary to have a sufficiently thick membrane to limit this diffusion phenomenon,

especially when operating pressures are much higher than atmospheric pressure.

3.1. Classification of membranes

In PEM electrolyze technology, the development and elaboration of performant membrane material is still the core of research. The membranes used in PEMWE can be categorized based on the type of material used to synthesize the membrane. The two main categories of PEMs are perfluorinated membranes and hydrocarbon-based membranes (non-fluorinated).

Perfluorinated membranes, such as Nafion®, are the PEMs that are most frequently used. They have a backbone consisting of perfluorinated polymers and sulfonic acid groups that allow proton transport. As an alternative to perfluorinated barriers, hydrocarbon-based membranes are composed of substances such as sulfonated poly(ether ether ketone) (SPEEK). These electrolytes have the advantage of being less expensive than perfluorinated membranes, but they generally have lower proton conductivity and chemical tolerance [67–69].

PEMs can also be classified based on their structure, which can be either homogeneous or heterogeneous. Homogeneous membranes are made of a single material, while heterogeneous membranes consist of multiple layers of different materials. Heterogeneous membranes are designed to improve membrane performance by combining the benefits of different materials, such as high proton conductivity and low gas permeability [37].

Acidic perfluorosulfonic (PFSA) and non-fluorinated membranes are employed in a large range of PEMs, but their performance is reduced above 90°C and at low relative humidity [67]. Therefore, to enhance the functionality of these separators, research has been conducted to introduce additional substances into the polymer matrix.

Membranes that are fully fluorinated, partially fluorinated, and non-fluorinated are the different categories of polymer electrolytes that have been researched, as shown in Fig. 3.
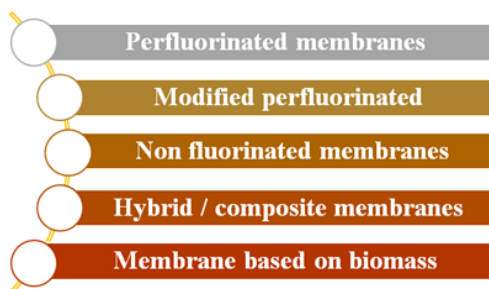

Fig. 3. Classification of the electrolyte membranes.Source: Authors

3.1.1. Perfluorinated membranes

One of the most essential aspects of PEM electrolysis is the membrane, and the most prominent categories are those made of perfluorosulfonic acids, such as Nafion and Flemion. Nafion is a sulfonated tetrafluoroethylene-based polymer with the chemical formula $C_nF_{2n+1} SO_3H$ that was created by DuPont in the late 1960s [37]. They are recognized for their significant stability in acid medium and strong proton conductivity. The membrane is an ionomer, a thermoplastic polymer that differs from polyelectrolytes by the percentage of ionic groups. As depicted in Fig. 4, the PFSA is divided into three key sections: (1) a polytetrafluoroethylene-like backbone (PTFE),
(2) the $–O–CF_2–CF–O–CF_2–CF_2–$side chains that communicate the backbone and the last section, and (3) ion clusters in the third area composed of sulfonic acid ions [70].

The third region's hydrogen ions become mobile by forming bonds with water molecules when the membrane is hydrated, and they migrate between sulfonic acid groups [69].
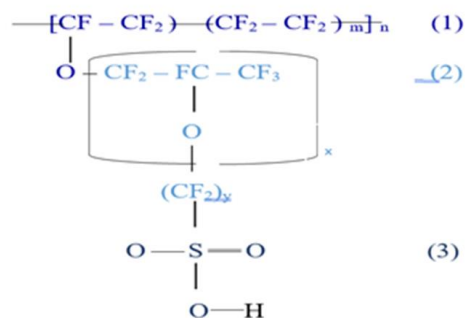

Fig. 4. General structure of PFSA membrane. Source: Authors

Membranes made of perfluorosulfonic acid (PFSA) distinguish for their superior performance, electrochemical stability, satisfactory mechanical properties, and quick start. As a result, improving perfluorosulfonic acid membranes and ionomers is essential to enhancing membrane electrode assemblies' performance at real current densities. According to the length of the side chain and the presence of -CF₃, the PFSA electrolyte are classified into long-side chain (LSC) membranes and short-side chain (SSC) membranes [70–76]. In this context, alternative PFSA barriers with shorter pendant side chains have been created, and several of them, including those from Asahi Chemical (Aciplex), Asahi Glass (Flemions), 3MTM, FuMA-Tech (Fumions), and Solvay-Solexis, are now commercially or experimentally accessible (Aquivion). The distance of the perfluorovinyl ether side chain, the presence or absence of the pendant -CF₃ group, the molar ratio of TFE, and the side chain functionalized TFE are some of the characteristics that differentiate these products from one another [63,64]. For instance, a side chain with a shorter length and no pendant CF₃ group produces a polymer with a higher glass transition temperature and crystallinity at the same weight as the polymer (EW). Various polymers, particularly Fumapem, Flemion, and Aciplex, are exploited. These materials are significant for their good characteristics, they differ from Nafion® by the length of the side chain and the distance between two of these chains in the main chain.

The highly recommended Nafion® membranes used in PEM water electrolyzes currently are Nafion® 115 and 117, as these electrolytes types offer considerable advantages, the membrane must always remain saturated with water to allow the movement of H⁺ associated with the sulfonate groups.

Membranes known as Aquivion® from the manufacturer Solvay can also be used. These are also perfluorosulphonated but have shorter pendant chains than Nafion®. They are also characterized by a higher crystallinity and glass transition temperature [65].

Solvay Specialty Polymers has developed a short-side-chain as shown in Fig. 5 (SSC) perfluorinated ionomer with no fluoroether group in the pendant side-chain, comprising only two CF₂ groups, chemically stabilized perfluorosulfonic acid membrane has an equivalent weight of 870g/eq [64].

As compared to long-side-chain (LSC) polymers at equal weight, this ionomer is identified with better crystallinity and a higher glass transition temperature. Aquivion® has been shown to have a glass transition temperature (T_g) in the dry state of 127°C contrary to 67°C for Nafion® [77]. Under humidified conditions, ionic exchanges are facilitated by the presence of water, causing the T_g to rise correspondingly.

These PFSA membranes do, however, come with a few disadvantages and limitations, including expensive prices, poor conductivity at low water levels, poor mechanical strength at higher temperatures, and low glass transition temperatures. In order to create these membranes, which can function at temperatures above 100°C, it is necessary to modify the existing ones by incorporating additional hygroscopic inorganic particles or by creating innovative polymer systems [32, 63].

There are specific parameters according to which membranes are classified [67]:
- The shape (membrane, dispersion, granules, and pellets).
- The thickness of the membrane.
- The manufacturing processes.
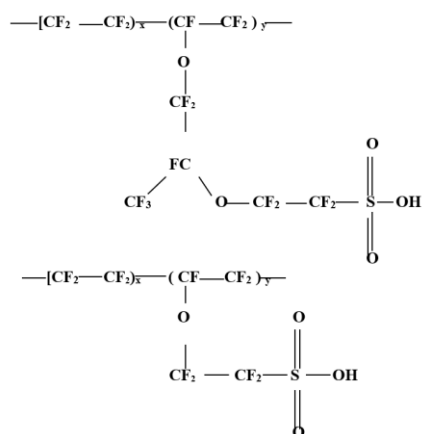- Teflon reinforcement.

Fig. 5. Polymer composition for long-side chain and short-side chain.

There are several commercially available perfluorinated membranes used in (PEMWE) [32, 37, 72–76, 63–65, 67–71] (Table 1):

- *Nafion*: This is the most used perfluorinated electrolyte. It is produced by the chemical company DuPont and is made up of a perfluorinated backbone with sulfonic acid groups attached to it. Nafion membranes have excellent proton conductivity, good mechanical strength, and high chemical stability.

- *Flemion*: It is produced by the Japanese company Asahi Glass Co. and is like Nafion in its chemical structure. Although Flemion membranes have strong mechanical durability and high proton conductivity, they are less chemically stable than Nafion.

- *Aciplex*: This is a perfluorinated membrane produced by Solvay, a Belgian chemical company. It has a similar chemical structure to Nafion but with shorter side chains. Aciplex is less chemically stable than Nafion.

- *Dowex*: This is a perfluorinated membrane produced by Dow Chemical. It has a chemical structure similar to Nafion but with a lower degree of sulfonation. Dowex membranes have lower proton conductivity than Nafion but are more mechanically stable.

- *Gore-Select*: This is a perfluorinated membrane produced by Gore, an American manufacturing company. It has a chemical structure similar to Nafion but with a higher degree of fluorination.

Table 1
Different types of perfluorinated commercial membranes [70].

Name	Parameters	EW	Thickness (mm)
Nafion117 Nafion115 Nafion112	m=1, x=5-13.5 n= 2, y= 1	1100 1100 1100	175 125 80
Flemion–T Flemion–S Flemion–R	m=0,1, n= 1 -5	1000 1000 1000	120 80 50
Aciplex-S	m=0, n=2 –5, x=1.5 -14	1000/1200	25/100

Perfluorinated membranes are well known for their excellent performance, they have good ion conductivity, excellent thermal and mechanical resistance, and good chemical resistance. Additionally, they exhibit low gas crossover and are impermeable to liquid water, which is essential for maintaining efficient permeability across the electrolyte [64]. They are widely used in laboratory settings, and they offer excellent performance in terms of current density and energy efficiency, making them a popular choice for PEM water decomposition experiments. Yet, the high cost of perfluorinated membranes is a major concern, and their performance can be negatively affected by high temperature and low humidity conditions. To overcome these limitations, research efforts have been directed toward developing new perfluorinated membrane formulations with improved properties and reducing their thickness to minimize the ohmic resistance in the system [67]. Non-fluorinated and partially fluorinated membranes have also been considered potential replacements for perfluorinated electrolytes, but their performance is still inferior in terms of mechanical and chemical endurance, ion conductivity, and gas crossover resistance. Therefore, despite their high cost, perfluorinated membranes remain the most widely used materials in PEMWE applications due to their superior performance and reliability.

Despite these challenges, perfluorinated membranes remain a key component in many laboratory-scale PEMWE systems, and ongoing research aims to further optimize their performance and address their limitations [69].

3.1.2. Modified/reinforced perfluorinated membranes

Significant endeavors are being done to improve the performance and efficiency of separator electrolytes, lower prices, and provide high-temperature operation to address issues related to the use of perfluorosulfonic acid (PFSA) membranes. The objective of elaborating composite membranes is to increase thermomechanical resistance through polymer/composite interactions. The two suggested alternatives are either adjusting PFSA membranes by incorporating new materials or employing a non-aqueous, low-volatile solution that accomplishes a similar function as water. The high conductivity of ions in Nafion selective barriers of water dissociation cells can be achieved in a solvent environment by replacing pure water with a non-aqueous, low-volatility solvent, such as water-organic mixtures, alcohols, organic acids, and aprotic dipolar solvents [32, 37, 72]. It is preferable to use thinner membranes to maintain water management during cell operation. The thinness of the membrane depends on the reduction of internal resistance [28, 56, 78, 79]. However, depending on how the electrolysis cell is configured to function (high temperature), the reduction of mechanical resistance represents a challenge for the development of thinner membranes [37]. To solve this problem, the reinforcement of PFSA composite membranes is a major element in achieving this challenge. This development is achieved by reinforcing materials such as polytetrafluoroethylene (PTFE). Among the most used and hydrophilic inorganic particles are silica (SiO_2), titanium dioxide (TiO_2), zirconium dioxide (ZrO_2), or hafnium dioxide (HfO_2). The effectiveness of Nafion-silica polymeric electrolyte is substantially higher than Nafion and can be observed according to Nafion/SiO_2> Nafion/ZrO_2> Nafion/WO_3> Nafion/T_iO_2 [80–84]. However, the development of these composite polymers is restrained by a significant loss in mechanical strength.

The comparison between altered Nafion and different inorganic substances/fillers, such as zirconium phosphate, titanium phosphate, cesium phosphate, and heteropolyacids, are highlighted in Table 2. The modification and development of these modified membranes have shown good results for the operation of (PEMWE) cells at high temperatures [85].

Table 2
Different types of modified/reinforced Perfluorinated membranes [84].

Membranes	Water uptake %	Conductivity (S/cm) [RH 100%]
Nafion®/SiO_2	34	$1.07 \times 10-2$
Nafion®/ZrO_2	24	$2 \times 10-2$
Nafion®/sulfated ZrO_2	27	$2.3 \times 10-1$

Modified or reinforced perfluorinated PEM have shown promising performance in laboratory-scale PEMWEs. These membranes are designed to overcome the limitations of traditional perfluorinated membranes. Reinforcement can be achieved through the incorporation of inorganic substances, such as silica or zirconia, which improve mechanical characteristics and proton conductivity. Additionally, modification of the chemical structure of the perfluorinated backbone can improve thermal stability and ion transport. Yet, the production of these modified membranes can be complex and expensive, limiting their practical applications. Further research is needed to optimize the performance and cost-effectiveness of these membranes for large-scale industrial use [85, 86].

3.1.3. Non-fluorinated membranes

Non-fluorinated polymeric membranes are a promising alternative under development, have a price reduction of the MEA assembly as its primary objective, and develop a material suitable for the operating conditions of the cell. Unlike traditional fluorinated membranes, which are made from perfluorinated sulfonic acid (PFSA) polymers, non-fluorinated membranes are made from alternative materials that do not contain any fluorine atoms. Several materials can serve as polymer backbones for proton-conducting polymer electrolytes [87, 88], such as (a) polysulfones (PSF), which are aromatic polymers characterized by appropriate resistance to hydrolysis and oxidation; and (b) polyetheretherketone (PEEK), which have the main advantage of high mechanical properties due to their polyaromatic backbone. The characteristics of PEEK membranes synthesized directly from sulfonated monomers are significantly superior to those of post-sulfonated PEEK [89].

There is no specific estimate for the proton circulation of this material, as it depends on several factors, including the selection of casting solvent, sulfonation process, level of sulfonation, relative humidity, and heat [89].

Sulfonated PEEK has some advantages over Nafion as an alternative polymer. The most well-known and commonly used sulfonated PEEK is Vichex PEEK, which is characterized by a temperature T_g of 143°C and a fusion temperature T_f of 334°C. However, it has some disadvantages such as difficulty in modifying it chemically due to its low solubility in organic solvents. At 80°C and 100% humidity, the conductivity is 10^{-2} S.cm^{-1}, which is lower than that of Nafion® under the same circumstances. Moreover, the structure of SPEEK permits the incorporation of polar sites, which contributes to increasing water absorption [90, 91].

Several other materials, such as poly(benzimidazole) functionalized or doped with acid, are under development. Polymer blend technology could be an effective solution for developing innovative membrane materials. A combination of materials offers numerous degrees of freedom in comparison to a one-component polymer, which enables the material to be adapted to the requirements of the membrane and the operating environment [89–91]. This blend is important and effective since it is possible to combine two materials that may have very different qualities. For example, it is possible to blend a material that is characterized by good mechanical properties with another material that is characterized by high flexibility [79]. Table 3 shows Different types of non-modified Perfluorinated membranes.

Polymer blend membranes are a combination of polymeric nitrogen with polymeric sulfonic acids. Proton exchange membranes made of polybenzimidazole (PBI) are among the most widely used acid-base polymer blends. They are highly effective non-fluorinated membranes with good thermal and mechanical tolerance at elevated temperatures, high proton conductivity, and low electro-osmosis, and they can function at high temperatures (T = 200°C). Additionally, they are low-cost compared to Nafion/perfluorinated ionomers [85, 87–91]. These membranes are extremely heat resistant and have a high proton conductivity; their cracking temperatures range from 270 to 350 °C [91].

Table 3
Different types of non-modified Perfluorinated membranes [84].

Type of membrane	Electrolyte Thickness (μm)	Conductivity (S/cm) [RH 100%]
Sulfonated polyimide	70	0.004 - 0.02
S-PEEK- aminated polysulfone blend	29	0.3
Phosphoric acid-doped sulfonated polysulfone	80-110	0.3

3.1.4. Hybrid \ composite membranes

The different types of polymers mentioned above have several advantages as PEMWE membranes, however, they have serious inconveniences that limit the development and commercialization of this hydrogen production process. One of the major problems is the low ion conductivity at high temperatures as a result of the low water content under these conditions. To solve this problem and boost the membrane's efficacy and effectiveness, various studies have concentrated on the evolution and fabrication of alternative high-achievement membranes. To this purpose, several approaches have been envisaged, like the use of new polymers or composite materials.

The term "Composite" or "hybrid material" are created by combining the polymer with other materials, such as inorganic particles (e.g. silica or titanium dioxide), carbon nano-tubes, or other polymers, it refers to a substance that contains two or even more molecularly combined substances, at least one of them is organic and the second one is inorganic [92, 93].

There are two primary types of inorganic-organic composite membranes: membranes made of less-proton conducting inorganic particles and proton conductive polymers, as well as membranes made of organic polymers and proton conductive particles [92, 93].

Proton exchange membranes have a special structural feature that consists of a system of nanopores and channels interconnecting the pores, the size of which varies depending on how hydrated the materials are. The incorporation of nanoparticles of various inorganic or macromolecular compounds into the pores may greatly increase the electrochemical properties, heat resistance, and mechanical characteristics of these materials. Various ways of realizing these membranes exist, such as the addition of

nanoparticles to boost the characteristics of Nafion [92–94], the process of preparing these ameliorations is simple because it is based on the dispersion of the inorganic charge, which is most often in the form of clays, Sepiolite, Halloysite, oxides (TiO$_2$, SnO$_2$, ZrO$_2$) or carbon nanotubes [51] within a polymer matrix previously dissolved in water or an organic solvent. The second panel is a blend of polymers with different properties in order to improve certain assets such as thermal resistance, mechanical properties, water retention, or proton conductivity values. These hybrid organic/inorganic membranes will be grouped into three categories, MH based on an aromatic polymer containing a hybrid conductive network from inorganic polymer, inorganic polymer functionalized by sulfonic and phosphonic functions, Organic/inorganic MH composed from non-conductive fluorinated polymer [94].

Based on this, novel composite membranes made of polymers with little or no proton conductivity are created, some of which have chemical and mechanical stability comparable to or superior to the traditional electrolyte.

By combining ferroxane and polyvinyl alcohol (PVA) nanoparticles, Zhang et al. [95] created proton-conducting composite membranes by coupling the strong proton conductivity of ferroxane and the favorable mechanical characteristics of PVA, the invention of a hybrid electrolyte with the potential to be used in PEMWE systems is ensured. The development of innovative electrolytes based on the principle of mixing one or more materials can have an important impact on accelerating the use of green hydrogen at the industrial level.

3.1.5 Membrane Based on Biomass

Membranes based on biomass are an emerging class of proton exchange membranes (PEMs) that are derived from renewable biomass resources such as lignocellulose, chitosan, and other natural polymers. Biomass-based PEMs have gained interest as a more sustainable and environmentally friendly alternative to traditional perfluorinated PEMs, which are derived from non-renewable and potentially harmful sources.

- **Based on carbon**

The interest in creating PEMs based on carbon materials has risen during the past few years, which are more affordable, sustainable, and environmentally friendly. They have shown promising properties. Firstly, they are more affordable and sustainable as carbon is abundant and inexpensive compared to the rare and expensive fluorinated monomers used in perfluorinated PEMs. Secondly, carbon-based PEMs have a lower environmental impact as they do not contain perfluorinated compounds that are persistent in the environment and can cause harm to wildlife and humans. Additionally, carbon-based PEMs can be recycled or disposed of more easily compared to perfluorinated membranes [96–98].

Carbon-based PEMs can be synthesized from a variety of carbonaceous materials, including graphene oxide, carbon nanotubes, and activated carbon [99]. Graphene oxide (GO) is a promising material for carbon-based PEMs due to its similar properties to PFSA. GO can be easily functionalized with sulfonic acid groups, which improve its proton conductivity by increasing the number of proton exchange sites. Carbon nanotubes (CNTs) are another potential material for carbon-based PEMs due to their high aspect ratio, which provides a large surface area for proton exchange [96–100]. CNTs can be combined with amino groups, which enhance their proton conductivity and selectivity. Activated carbon (AC) is a widely available material that has shown promising properties for carbon-based PEMs. As a result of its large porosity and large surface area, AC contains an abundance of proton exchange-active sites. AC can be functionalized with sulfonic acid or amino groups to enhance its proton conductivity and selectivity. Overall, carbon-based PEMs have the potential to offer a more sustainable and cost-effective alternative to traditional perfluorinated PEMs, and ongoing research is focused on optimizing their properties for various electrochemical applications [96]–[100].

- **Based on nanocellulose**

Lignocellulosic waste is a material derived from lignocellulosic biomass, such as straw, sawdust, bagasse, and other non-food plant materials. These materials could be synthesized into PEMs based on naturally occurring polymers including cellulose, lignin, and hemicellulose, which are fundamental components of plant cell walls. Nanocellulose has adequate properties such as high surface area, high strength, and excellent water retention, which make it a promising material for PEMs [101–103]. Nanocellulose is produced from cellulose, which is a natural polymer. The

production of nanocellulose involves the fragmentation of these cellulose fibers into nanometric particles. This can be achieved in different ways, including mechanical, chemical, and enzymatic methods.

Several approaches have been proposed for fabricating nanocellulose-based PEMs, including:

- Composite membranes: nanocellulose can be blended with other materials such as chitosan, polyvinyl alcohol, or polyethylene glycol to form composite membranes. These are employed to strengthen the mechanical resistance and water retention properties of the membrane. The blending process involves dispersing nanocellulose in a solvent or water followed by adding the other material and stirring to obtain a homogenous mixture. The resulting mixture can then be cast into a film or membrane using techniques such as solvent casting or spin coating. Composite membranes have shown good proton conductivity and mechanical properties. For example, a composite membrane made of nanocellulose and chitosan has shown a proton conductivity of 0.004 S/cm at 80°C and 100% relative humidity (RH) [104, 105]. Another composite membrane made of nanocellulose and polyvinyl alcohol has shown 0.012 S/cm at 100% RH and room temperature [104, 105].

- Self-standing membranes: Nanocellulose can be used alone to form self-standing membranes through methods such as vacuum filtration, spin coating, or layer-by-layer assembly. In vacuum filtration, a suspension of nanocellulose in water or a solvent is poured onto a filter paper or membrane, and the water or solvent is removed under vacuum to obtain a self-standing membrane. Spin coating involves depositing a layer of nanocellulose on a substrate by spinning at high speed [101–103, 106, 107]. Layer-by-layer assembly involves depositing multiple layers of nanocellulose on a substrate, alternating with a polyelectrolyte such as polyethyleneimine or poly(styrenesulfonate) [101–103].

- Surface modification: involves introducing functional groups such as carboxyl, sulfonic, or amino groups to the surface of nanocellulose to improve its proton conductivity and water retention. This can be achieved by treating nanocellulose with chemicals such as sulfuric acid, sodium hydroxide, or epichlorohydrin [101–103]. Surface-modified nanocellulose has shown improved proton conductivity and water retention properties. For example, a surface-modified nanocellulose with sulfonic acid groups has shown 0.042 S/cm at 80°C and 100% RH [108].

Overall, the development of nitrocellulose-based PEMs instability early stages, and some challenges need to be addressed such as improving the stability and decreasing the cost of the membranes. However, the unique properties of nanocellulose offer a promising alternative to traditional PEM materials.

3.2. Essential transport phenomena in the membrane

Fig. 6 shows the different stages and essential processes of transport phenomena. The membrane's function in an active cell is to effectively transport ions and water, reject electrons, and separate reactant gases. Protons pass through water channels in the PEM electrolysis cell. Thus, it's crucial to manage the water molecules in the membranes that swell to determine the proton conductivity. As the water activity of the membrane significantly impacts the transportation of protons, water circulation modeling is also essential.
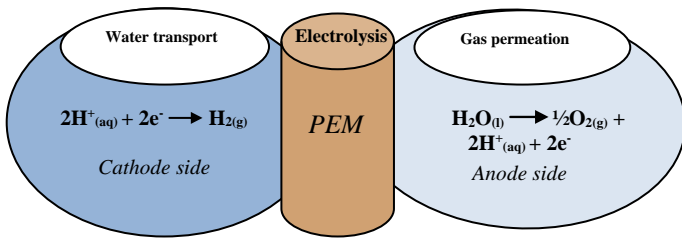

Fig. 6. Important membrane transport phenomenon. Source: Authors

3.2.1. Water transport

The amount of water is a way to characterize the H_2O absorption of the solid electrolyte.

This is represented by the λ_m which is defined as the number of absorbed water molecules (n_{H2O}) divided by the number of sulfonate groups. ($n_{SO3–}$) [52].

$$\lambda_m = \frac{n_{H_2O}}{n_{SO_3^-}} \quad (18)$$

It can also be defined in terms of the equivalent weight EW [g mol^{-1}], the dry density of the membrane ρ_{dry} [g.m^{-3}], and the concentration of H_2O molecules in the membrane C_{H2O}(mol.m^3) [52]:

$$\lambda_m = \frac{EW}{\rho_{dry}} C_{H_2O} \quad (19)$$

Sorption, transport, and desorption inside the electrolyte barrier are necessary for H_2O to pass through. The PFSA polymer's chemical structure regulates the membrane's physical qualities like porosity, tortuosity, and the structure of its ionic zones, while the manufacturing process utilized to create the membrane dictates its overall water permeability [109].

By measuring the H_2O flux under a chemical potential gradient resulting from an alteration in either water concentration or pressure; it is possible to determine the membrane's permeability. [110]. The system's efficiency in "dry" environments is enhanced by a faster rate of water flow across the membranes. Since protons and water molecules move through the same tortuous, hydrophilic pathways, the rates of water penetration and effective proton mobility are dynamically related [27, 28]. It is essential to note that net water movement occurs both on the membrane's surface and, less commonly, inside the electrolyte.

Ideally, water flows only through the anode channel, but some of the H_2O passes through the electrolyte interface into the anode channel. Three distinct factors cause water to pass through the membrane [110–114]. Water diffusion is the initial consideration; it is mostly non-linear and is impacted by temperature, gradient, and membrane structure. From the anode to the cathode, water circulates, from high to low-concentration regions. In other words, to create protons and oxygen gas, most of the water undergoes the oxygen evolution process. Therefore, the diffusion phenomenon is a mechanism that transfers a small quantity of water through PEM and this is justified by the substantial pressure inequalities between the both positive and negative sides. The PEMWE's negative side is maintained at a relatively constant 1 bar while the cathode side generates hydrogen at a maximum pressure of 70 bars [27, 28, 110–114].

The second process, related to electro-osmotic water drag, is significantly impacted by the current density and membrane hydration level. By measuring how many moles of H_2O are pulled by each mole of H^+ ions, electro-osmotic drag can be used to measure the quantity of water that is transported across the selective electrolyte.

The third mechanism is the pressure gradient, which is generated by the osmotic pressure gradient and the hydraulic component (Darcy flow). The permeability of the membrane determines the water flow resulting from the pressure differential between the two sides, and this flow is calculated using Darcy's Law [115–117].

3.2.2. Proton conductivity

Ion transport in the PEMWE membrane is mainly achieved by conduction. However, to complete the electrochemical process, the phenomenon of proton migration is significant, as it impacts how protons move across the polymeric membrane. It represents one of the most crucial elements for identifying the limiting current density and, eventually, establishing how an electrolyzer function. EW (number of charge carriers), hydration number, polymer structure, membrane thickness, and temperature all significantly influence ionic conductivity in PFSA membranes [111, 112, 118]. Furthermore, it (measured in S.cm^{-1}) depends directly on the water content and temperature and is a key characteristic for assessing a membrane's performance or utility as a candidate for PEMWE. Moreover, the ability of the membrane to store water and the environment's humidity have a significant influence on conductivity.

This dependence is generally described by an Arrhenius law [52]:

$$\sigma_m = A\exp(-\frac{E_A}{RT_m}) \quad (20)$$

where A is the parameter that depends on the water content, E_A represents the activation energy for ion conduction, R perfect gas constant, and T_m is the temperature, the pretreatment of the membrane has an impact on these characteristics as well.

Furthermore, gases and water can pass through these membranes, causing the appearance of hydrogen on the oxygen section and vice versa. The term

used to describe this mechanism is gas crossover. Two modes ensure the transport of protons: the Grotthuss mechanism and the Vehicle mechanism via diffusion [119–122].

The Grotthuss method involves the creation of hydronium ions (H_3O^+), which transport protons from one ionic site of hydrolysis to another. However, in the second process, the influence of concentration variation on diffusion and electro-osmotic action is what transports the hydronium ions. Since the diffusion step of the Grotthuss mechanism is quicker than that of the second mechanism, it dominates proton conduction [121, 122].

3.2.3. Ion transport

In addition to protons and water molecules, other ions, such as hydroxide ions (OH^-) may be generated during the electrolysis process and transported through the PEM. These ions can contribute to the cathode's development of hydroxide ions, which can affect the overall efficiency of the PEMWE system [27]. Therefore, it is important to have selective ion transport in the PEM to prevent contamination of the electrolyte solution and maintain high efficiency. Selective ion transport in the PEM can be achieved by controlling the size and charge of the pores in the membrane. The pores should be small enough to prevent the transport of larger ions that could contaminate the electrolyte solution, while still allowing for the transport of protons and other smaller ions. The charge of the pores can also be controlled to selectively allow the transport of certain ions while repelling others [118, 123, 124].

Ion transport in the PEM occurs through two primary mechanisms: diffusion and electroosmotic drag. Diffusion is the movement of ions from high concentration to low concentration, while electroosmotic drag is the action of an electric field on the mobility of ions. These mechanisms can be managed by adjusting the properties of the PEM, such as the particle size, charge, and thickness [119, 123, 124].

Research is ongoing to develop new PEM materials and optimize system designs that can improve selective ion transport and prevent contamination of the electrolyte solution. By improving ion transport in the PEM, PEMWE systems can operate more efficiently and produce high-quality hydrogen for a wide range of applications.

3.3. Degradation and durability of membranes

The most promising membranes for producing hydrogen are proton electrolyte membranes (PEMs), which have reasonable conductivity at low temperatures. However, there are still issues preventing the widespread use of PEM production. The first challenge concerns operating temperature. Water electrolysis cells with Nafion® type membranes cannot exceed a maximum temperature of 100°C [12]. In practice, the acceptable operating temperature ranges around 60 and 80°C [12]. However, at temperatures above these levels, the membranes risk losing their mechanical properties. The second challenge relates to humidity. It is necessary that the membrane remain constantly wet, as the handling of water is a key factor in the PEM cell membrane. Water represents the reactant, which must be distributed uniformly toward the catalytic sites to enable the displacement of H^+ ions [119]. Otherwise, current circulation in the cell will stop. Conversely, if the membrane becomes too dry, it becomes much more fragile and can break [125]. Membrane deterioration, which may be divided into mechanical, thermal, and chemical/electrochemical types, is one of the principal reasons that reduce a stack's endurance.

3.3.1. Mechanical and thermal deterioration

When electrolysis is used for more than 1000 hours, the membrane often encounters significant difficulties, such as mechanical troubles like cracks, tears, pressure from the reactants, and stress. As a result, mechanical deterioration is induced by repetitive expansion and contraction related to variations in wet and dry conditions that compromise the membrane's integrity [126]. These phenomena are related and due to [126–128]:

-The compression of the electrolyte during operation.

-The presence of multiple components of different materials forming the membrane electrode assembly, with excessive forces exerted on the bipolar plate channels causing compression that leads to degradation. The irregular compression of current collectors, which allows some titanium ions to penetrate the system, can also degrade the membrane.

-In contrast to chemical attack, mechanical failure is more frequent at high working pressures because the electrolyte is susceptible to creep and the cross-penetration of gases at higher pressures.

-A high water flow in the cell leads to the accumulation of pressure, which causes degradation.

-Variations in the membrane's relative humidity are essential to the deterioration of the membrane.

- Minimal current frequencies when the electrolysis is working at a high temperature cause the membrane's solubility and mobility to decrease, degrading cell operation.

-A bad distribution of the current lines can lead to the apparition of hot spots that speed up the deterioration and even cause holes.

-To ensure highly efficient functioning, the PFSA membrane typically operates at a suitable operating temperature of approximately 80°C.

3.3.2. Chemical / electrochemical degradation

Chemical degradation represents one of the major obstacles to sustainable and long-term operations and is a significant issue in perfluorosulfonic acid (PFSA) membrane failure. The thinning of the membrane and the chemical interaction between it and the hostile radical species produced during the electrolysis operation can affect how durable the membrane is. Even though PFSA membranes are made of a chemically inert fluorocarbon structure like Teflon, which is crucial for stability, the electrolyte is susceptible to chemical deterioration [16].

-*Thinning of membranes* is necessary to limit and reduce the ohmic drop and the size of the system, and the membrane must be as thin as possible. However, this membrane is not perfectly impermeable to gases, so some of the reactants produced can pass through it. Indicating that the crossover permeability of gas improves with temperature and drops down with current density, the continuous oxygen crossover occurs throughout the electrolysis process. According to Grigoriev et al. [125], the electrolyte thickness decreases by almost 75% following a 5500-hour long-term test.

Conventionally, compared to oxygen, hydrogen permeates anodes from cathodes more effectively. Consequently, oxygen infiltrating at the cathode competes with the hydrogen production reaction, which leads to the process used to manufacture hydrogen peroxide at the surfaces of the platinum electrode. This is responsible for the degradability of the membrane [37, 125, 129]. The main mechanism of chemical degradation is an attack by hydroxyl radicals (OH^-) related to the development of hydrogen peroxide (H_2O_2) [130]. In fact, when O_2 penetrates through the membrane, the subsequent reaction results in the formation of H_2O_2.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (21)$$
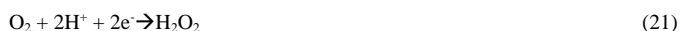
This peroxide is catalyzed by the presence of metal cations, dissociating into radicals (OH^-) through several mechanisms. These radicals then attack the principal and secondary chains of PFSA, leading to a loss of membrane thickness [129]. Metal cations can come from platinum dissolution, bipolar plate oxidation, or feed water. This thinning of the polymer electrolyte leads to an increase in the permeation phenomenon, which can cause the electrolyzer to stop operating [129, 131]. The presence of oxidizing species causes the deterioration of the perfluorosulfonic acid backbone of the membrane, resulting in the release of fluoride and sulfur and thinning of the membrane. Therefore, the fluoride release amount (FRR) and sulfur emission rate approaches can be used to examine chemical degradation [37, 125, 129, 131]. This phenomenon of membrane permeation to gases can be problematic. Beyond 4 vol. % of dihydrogen in dioxygen, the mixture becomes explosive [91]. Therefore, it is necessary to have a sufficiently thick membrane to limit this diffusion phenomenon, which is particularly accentuated when operating pressures are much higher than atmospheric pressure.

- *Contamination of metals:* several studies have demonstrated that the liquid-phase conductivity decreases whenever there are cations on the electrolyte. Corrosion leads to the formation of several metal ions, including Na^+, Li^+, Ca^{2+}, Cu^{2+}, Ni^{2+}, and Fe^{3+} [130]. These ions are considered contaminants that can affect the membrane's performance. These impurities cause high ohmic losses because most metal cations travel differently through the Nafion electrolyte than protons due to their higher affinity for sulfonic acid groups [129, 131]. What follows is a summary of the deterioration caused by poisoning: [37, 129–131]:

- Diffusion and permeation are initially used to dissolve the metal ions.

- Subsequently, these ions occupy the membrane's ion exchange sites. Since most of these ions have a higher affinity than H^+ for the sulfonic acid groups of Nafion, this affects the flow of metal cations in the electrolyte

compared to protons, which significantly impacts ionic conductivity when protons (H^+) are replaced by metal cations.

- Finally, metal ions' flexibility is substantially lower than that of H^+, resulting in the accumulation of ohmic losses.

3.3.3 Perspectives

The durability of the electrolyte in PEMWE is one of the serious problems encountered in its design and operation. To prevent mechanical and chemical membrane deterioration accompanied by electrolyte thinning, metal ions occupying exchange receptors, and corrosion caused by thermochemical processes, the following options should be considered [37, 125, 127–131]:

-The use of inert, non-conductive reinforcing materials, such as polymer fibers, to produce the membrane, as well as the conservation of the membrane edges in the sealing area, especially in cases of high mechanical loads required for sealing at high temperatures, are suggested remedies that could minimize these difficulties.

-Particular attention has been given to the synthesis of membranes that can chemically tolerate peroxide radicals. One remedy is to create new membranes that are more chemically stable. It is also advised to use materials with high resistance to corrosive content when creating membranes. Finally, it is recommended to use distilled water to reduce the membrane's susceptibility to poisoning. Innovative electrolytes can also be manufactured by including free radical inhibitors and stabilizers, such as hindered amines or antioxidants.

- To avoid the degradation of perfluorinated sulfonic membranes under the effect of free radicals, the incorporation of MnO_2 nanocomposites allows the process of hydrogen peroxide degradation and the elimination of free radicals without causing major degradation in the performance of the electrolyte [129].

4. Discussion

The critical review of electrolyte membrane evaluation for PEMWE highlights the important role of PEM membranes in the effectiveness and robustness of the electrolyzing cell. The review emphasizes the need for a comprehensive understanding of the functioning, performance, and limitations of the electrolyte membrane. There are several methods used to evaluate the performance of electrolyte membranes, these methods can provide valuable insights into the important aspects that influence the performance and durability of the electrolyte, such as chemical consistency, mechanical strength, and proton conductivity [132].

Here are some used methods [133–136]:

- *Conductivity measurements*: as said previously, conductivity is an important parameter for electrolyte membranes as it determines the rate of proton transport. Conductivity measurements determine the proton conductivity of the electrolyte membrane and can provide information on the membrane's ability to transport protons efficiently.

- *Thermal stability tests*: can be used to evaluate the stability of the membrane under varied temperatures and to determine the maximum temperature at which the membrane can operate without degradation. This information is critical for designing electrolyzer systems that operate at high temperatures.

- *Water uptake measurements*: can be used to evaluate the aptitude of the electrolyte membrane to absorb and retain water. This is important as water is necessary for the proton transportation process, and the membrane must maintain a balance between hydration and dehydration to function effectively.

- Mechanical strength tests: can be used to determine the longevity and mechanical stability of the electrolyte under different stress conditions, such as tension, compression, and bending.

- *Durability tests:* durability tests can be employed to measure stability over time and the performance of the electrolyte membrane under continuous operation.

Regarding the several classifications of membranes used and under development, Table 4 summarizes a comparison between them.

In summary, the choice of PEM for a PEMWE depends on various factors, including operating conditions, cost considerations, and performance requirements. Perfluorinated membranes offer excellent performance but are expensive and may have limited durability under harsh operating conditions. Modified perfluorinated membranes offer improved durability but may have lower performance. Non-fluorinated membranes offer lower cost and good stability but may have lower performance and mechanical strength. Hybrid and biomass-based membranes offer promising sustainability benefits, but

their performance and durability may vary depending on the specific composition and manufacturing process.

Table 4
Comparison between the membranes.

Property	Perfluorinated Membranes	Modified Perfluorinated Membranes	Non-Fluorinated Membranes
Proton conductivity	Extremely good	Good to moderate	Good
Chemical stability	Extremely good	Good	Good
Thermal stability	Moderate to Good	Excellent	Good to Excellent
Water uptake capacity	High	Moderate	Low to Moderate
Mechanical strength	Excellent	Good	Moderate
Cost	High	Moderate	Low
Durability	Limited	Good	Moderate to Good
Performance	Excellent	Good to moderate	Good

The implementation of the green hydrogen produced by PEMWE is strictly dependent on the development of the proton electrolyte membrane. Therefore, any improvements in the characterization of electrolyte membranes can have a considerable consequence on the overall performance of the technology. This can reduce the estimated quantity of energy necessary for producing green hydrogen, making the technology more cost-effective and environmentally friendly. In addition, improved membrane characterization can lead to the advancement of membranes that have higher resistance to deterioration. For the PEM electrolysis concept to be industrialized and widely exploited, there are still several challenges and problems that need to be remedied.

5. Conclusion

Today, the energy transition to green hydrogen has become a priority in energy strategies around the world; it is an efficient and innovative solution that will ensure the decarbonization of the industrial sector and the reduction of greenhouse gas emissions that causes climate change. Throughout this work, we have discussed that hydrogen is the future of the energy sector, it is promising, clean, and sustainable energy. After overcoming the problem and the solution, we highlighted the application of the water electrolysis mechanism, especially PEMWE, for the manufacturing of green hydrogen.

Afterward, we explored the general operating principles of PEMWE including thermodynamics and electrochemical aspects as well as the performance of the electrolyzer, and then we defined the component of the PEM cell, their functioning, and their operating conditions, also the main advantages and disadvantages. The final part highlights the generality of proton exchange membranes where we explained the classification of each type according to composition and operational condition, transfer activities in the electrolyte, and types of degradation of the latter along with some perspectives and solutions proposed to avoid and prevent the degradation of the proton electrolyte membrane.

As a result of the exhaustion of fossil fuels, environmental regulations, and the implementation of renewable energy sources, it is anticipated that the PEMWE hydrogen generation process will change and become more efficient over time. However, the main obstacles and challenges to the industrialization of PEMWE technology are its cost, degradability, and durability.

The deterioration of the membrane is one of the main barriers preventing the growth of the PEMWE, in addition, the majority of the cost of the electrolysis cell is accounted for by the cost of the polymeric membrane.

CRedit authorship contribution statement

Z. Hammi: Data curation; editing - original version; formal analysis.
N. Labjar: Analysis, methodology, supervision, and validation
E.M. Lotfi: Methodology and validation
S El. Hajjaji: Analysis, methodology, supervision, and validation

Declaration of Competing Interest

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

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