ChemEngineering

Review

An Analysis of the Conceptual and Functional Factors Affecting the Effectiveness of Proton-Exchange Membrane Water Electrolysis

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Abstract: Hydrogen has the potential to decarbonize the energy and industrial sectors in the future, mainly if it is generated by water electrolysis. The proton-exchange membrane water electrolysis (PEMWE) system is regarded as a propitious technology to produce green hydrogen from water using power supplied by renewable energy sources. It offers many benefits, such as high performance, high proton conductibility, quick response, compact size, and low working temperature. Many conceptual and functional parameters influence the effectiveness of PEM, including temperature, pressure of anode and cathode regions, water content and wideness of the layer, and cathode and anode exchange current density. In addition, the anodic half-reaction (known as the oxygen evolution reaction (OER)) and cathodic half-reaction (known as the hydrogen evolution reaction (HER)) perform an important function in the development of PEMWE. The current study aims to present these parameters and discuss their impacts on the performance of PEM. Also, the PEM efficiency is presented. The different methods used to enhance the scattering of OER electrocatalysts and minimize catalyst loading to minimize the price of PEMWE are also highlighted. Moreover, the alternative noble metals that could be used as electrocatalysts in HER and OER to minimize the cost of PEM are reviewed and presented.

Keywords: water electrolysis; oxygen evolution reaction; hydrogen evolution reaction; electrocatalyst

Citation: AlZohbi, G. An Analysis of the Conceptual and Functional Factors Affecting the Effectiveness of Proton-Exchange Membrane Water Electrolysis. *ChemEngineering* **2024**, *8*, 116. https://doi.org/10.3390/chemengineering8060116

Academic Editor: Luis M. Gandía

Received: 18 August 2024
Revised: 18 September 2024
Accepted: 23 September 2024
Published: 13 November 2024

1. Introduction

Nowadays, the major challenges affecting the world are global warming and climate change caused by the rise in the global population, as well as the massive exploration and use of fossil fuels. The energy sector is the main contributor to global warming, accounting for exceeding two-thirds of universal greenhouse gas emissions. The reduction in GHG emissions from the power sector through increasing the share of green and renewable energy resources is regarded as an efficient solution to cope with the effects of climate warming. Nevertheless, the irregularity of renewable energy slows down the full carbon depletion of the energy sector. Storing energy is viewed as a vital solution to increase the deployment of renewable energy by storing the energy during the high-supply period and reusing it during the high-demand period. Storing the energy in a Li-ion battery is a good option since it has high energy efficiency and can utilize existing charging infrastructure; however, energy density is low, and it has a limited charging rate, rendering it unfeasible for large applications. Recently, hydrogen has received more attention as a promising sustainable and carbon-neutral energy supply. Hydrogen has attractive advantages, such as an energy supply with a high-energy density of up to 140 MJ/kg, compared to hydrocarbon fuels, with an energy density of 50 MJ/kg. In addition, hydrogen has a high charging rate, making it practical to be used in large applications. Many renewable and non-renewable energy resources could be used to generate hydrogen-like fossil fuels, biomass, biological sources, and water electrolysis.

The hydrogen derived from water by using energy generated from renewable resources is known as green hydrogen. The use of green hydrogen to stock the surplus of energy generated from renewable energy sources in order to use it at peak periods is deemed an efficient technology thanks to its numerous benefits. Besides its potential to be used as energy storage, it is a sustainable and clean fuel with zero emissions; it can be used as fuel cells to generate electricity, it has high calorific combustion value, and it is able to fight against global warming since it can substitute the fossil fuels. Water electrolysis is used to produce green hydrogen by decomposing the water into hydrogen and oxygen. The operating principle of electrolysis is fundamentally similar, while electrolyzers are differentiated by the kind of electrolyte materials and the working temperature. The electrolyzer is categorized into two categories: a low-temperature electrolyzer and a high-temperature electrolyzer. The low-temperature electrolyzers are commercially available and involve a proton-exchange membrane (PEM), alkaline electrolysis, and an anion exchange membrane (AEM). A proton-exchange membrane (PEM) and alkaline water electrolysis are the only technologies that are commercially available [1]. However, the high-temperature electrolyzers are still in the research and development phase. The technology of AEMWE is mature and cheaper, but it has many issues related to slow start-up, several components, corrosion, and difficult maintenance.

The PEM electrolyzer has lately earned traction and popularity owing to its various advantages in comparison to conventional alkaline water electrolyzers. It is safer, with great reliability, high hydrogen purity, lower power usage, and operability at high current density [2,3]. Also, PEM water electrolysis is distinguished by its capability to accelerate and decelerate fast and a large working range of 0–100%, making it a functional solution to deal with the irregularity issues of renewable energy resources. Also, PEM water electrolysis is convenient for off-grid use, powerful, compact, features reduced maintenance, and is appropriate for small- to medium-sized industrial applications, whilst the cost of a PEM electrolyzer is higher compared to alkaline owing to the utilization of noble metals, such as Pt/Pd, as electrocatalysts. In addition, the large amount of water and its purification, which is demanded to run PEM water electrolysis, increases its capital cost. Also, a PEM electrolyzer experiences difficulties in terms of an acidic environment and low endurance. The cost of a PEM electrolyzer is primarily driven by the cost of the bipolar plate, which accounts for 48% of the total cost. Recently, several studies were performed to boost the performance and lower the price of PEM electrolysis by finding replacement bipolar plates, catalysts, and a PEM-based membrane electrode. Fundamentally, there are two methods to minimize the cost of PEMWE while keeping a high performance. Replacing expensive stack materials, like Ir and Ti, is one of the options to minimize the cost of PEMWE, but it affects the endurance and the efficiency of PEMWE. The second option, which is more realistic than the first one, is based on operating the electrolyzer under convenient circumstances to achieve a high rate of H_2 generation. The following operation approaches are essential for performance improvement:

- Increasing the current density to increase hydrogen generation rates.
- Increasing the working temperature to improve cell performance.
- Increasing the hydrogen output pressure to prevent the need for mechanical compressions and thus minimize costs and improve the efficiency of the system.

Ref. [4] examined and studied the lifespan, capital cost, and efficiency of PEMWE. The findings pointed out that a transference from an alkaline electrolysis membrane (AEM) to a PEMWE will happen by 2030, owing to its various benefits when it comes to coupling with renewable energy resources. In addition, a reduction in the investment cost has already been recorded by 2020 compared to 2016, and a reduction in price with the larger functional flexibility will achieve a commercial profit by 2030.

The current paper aims at presenting a review on a PEM water electrolyzer (PEMWE). The efficiency of PEMWE and the different conceptual and functional factors affect its performance are extensively discussed and presented in this paper. In addition, the recent developed technologies to enhance the efficiency of PEMWE are highlighted. This study might support researchers to enhance the efficiency of PEM by raising the amount of hydrogen generated and safety and lowering the price of hydrogen production.

2. Background of PEM Water Electrolysis

The PEM was initially launched in the 1960s by General Electric for fuel cell usage and then for electrolyzer usage [5]. In 1987, the first PEMWE was implemented by a metallurgical company (Stellram) in Nyon, Switzerland, which was intended to supply 20 $Nm^3 h^{-1}$ of hydrogen at a pressure of 1–2 bars. Currently, the PEMWE is used in many sectors like hydrogen generation, hydrogen welding, pure substance generation utilized in pure metals, electronic industry, and the metallurgy of alloys.

2.1. Operating Principle of PEMWE

The main components of PEMWE are the membrane electrode assembly (MEA), the compression plate, the gas diffusion layer (GDL), the anode and the cathode chambers, and the bipolar plates (BPP). The compression plate is formed from an aluminum alloy and employed to fix the whole electrolysis cell. The MEA comprises a proton-conducting layer coated with porous electrocatalyst layers on both the anode and cathode areas that present the essential component of the electrolyzer, in which water is broken down into gaseous hydrogen and oxygen by an electric current. The bipolar plates (BBP) are flat separator plates and used to conduct electric currsent between cells, equally spread air and fuel gas, eliminate heat from the active region, and avoid the seepage of gases and coolant. The gas diffusion layer (GDL), also known as the current collector PTL, is an electronic conductor between BPP and MEA. It is used to maintain an efficient mass transfer of gases and liquids between the BPP and the electrodes.

The working principle of PEMWE is based on applying an external supply of energy (a minimum potential of 1.23 V) through the electrochemical cell to kick off the electrochemical reactions at the cathode and the anode electrodes (Figure 1). In order to accelerate the reaction, catalysts should be utilized. The catalysts utilized are primarily a few noble metals, namely, the platinum and the iridium. The procedure commences by injecting water at the anode, and then the water molecules are decomposed into protons (H^+), oxygen, and electrons (e^-) at the anode via a dint of the electric field and catalyst. The water is transmitted from the path of the BPP to the catalyst coat on the layer through the current collector. After that, the protons stir to the cathode area through the MEA, which only permits the protons to spout. At the cathode side, an external power is used to incorporate the protons with the electrons aiming to compose hydrogen gas molecules. Electrons come from the catalyst coat on the anode region and permeate the current collector and BPP to reach the cathode region. The overall reaction, including the anode and cathode reactions, is presented below.

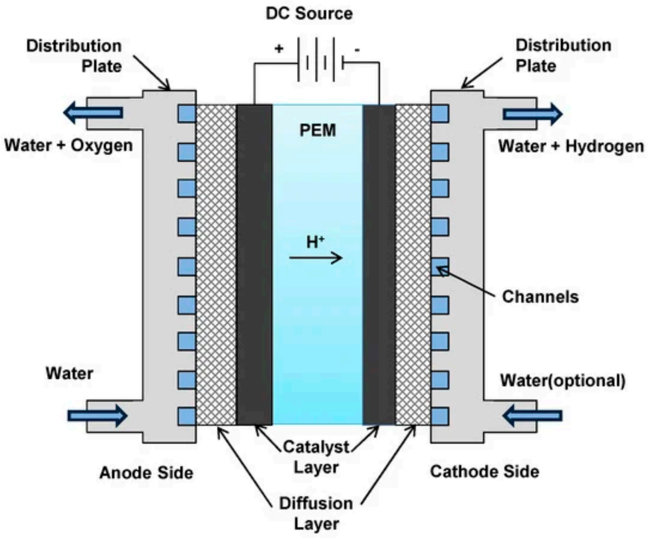


Figure 1. Visual representation of PEMWE [6].

The overall reaction is

$$\boldsymbol{2H_2O(l) \rightarrow 2H_2(g) + O_2(g)}$$

The anode reaction (oxidation) is

$$\boldsymbol{2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-}$$

The cathode reaction (oxidation) is

$$\boldsymbol{4H^+(aq) + 4e^- \rightarrow 2H_2(g)}$$

The use of noble metals, namely, IrO_2/RuO_2 in the oxygen evolution reaction (OER) at the anode and Pt/Pd in the hydrogen evolution reaction (HER) at the cathode, are the main drawbacks of PEMWE. The hydrogen and the oxygen molecules are not able to be merged owing to the impenetrability of the layer to oxygen and hydrogen molecules. Nevertheless, water is flowed with proton through the layer, and this situation is named electro-osmotic drag. The efficiency of PEMWE and the yield of hydrogen generation depends on the membrane, the temperature, the pressure, the cell voltage, and the current density. Additionally, membrane hydration is a critical factor affecting the PEMWE. For efficient proton conductivity and a higher cell efficiency, the membrane should maintain hydrated. Thus, efficient water management and proper pressure and temperature management should be considered in order to avoid dehydration of the membrane.

2.2. Types of Electrolyzer Performance

The component of electrolyzer efficiency comprises three efficiencies: hydrogen generation efficiency, Faradaic efficiency, and the effort needed to compress the output hydrogen gas.

- Hydrogen generation efficiency.

The process of decomposing water into hydrogen and oxygen in the electrolysis process requires energy. The magnitude of needed energy is assessed by the enthalpy change (ΔH), which is the combination of Gibbs free energy (ΔG) and heat energy. Gibbs free energy is utilized to estimate the lowest needed decomposition voltage to operate the electrochemical reaction given that it matches the demanded energy to make a water molecule using gases of oxygen and hydrogen. The evaluation of Gibbs free energy under a standard environment is performed using

$$\Delta \boldsymbol{G} = \boldsymbol{NFV_{reversible}} \tag{1}$$

where N is the number of involved electrons, F is the Faraday's constant (96,500 C·mol^{-1}), and $V_{reversi\text{ble}}$ is the reversible voltage, which is described as the lowest demanded voltage to break down the water into oxygen and hydrogen. It is equivalent to 1.23 V [7,8].

The entropy $T\Delta S$ presents the heat energy. The enthalpy variation is 85.84 kJmol^{-1} in standard circumstances. Consequently, the thermal-neutral voltage, which is the lowest demanded voltage for electrolysis, might evaluated by using the following [9]:

$$\boldsymbol{V_{TN}} = \frac{\boldsymbol{\Delta H}}{\boldsymbol{NF}} = \frac{\Delta \boldsymbol{G}}{\boldsymbol{NF}} + \frac{\boldsymbol{T\Delta S}}{\boldsymbol{NF}} = 1.48 \tag{2}$$

The used potential must transcend the reversible voltage to promote the charge transmission in the MEA of an electrolyzer, considering there is a proportional relation between the current density and the rate of hydrogen generation. The estimation of hydrogen generation efficiency is performed using the output of electrical energy transformed to chemical energy. Consequently, the estimation of hydrogen generation performance is performed by using the higher heating value of hydrogen. The calculation of hydrogen efficiency is performed by dividing the thermo-neutral voltage (V_{TN}) by the measured cell voltage (V_{cell}) [1]:

$$\eta_{p,H2} = \frac{V_{TN}}{V_{cell}} \tag{3}$$

The cell voltage relies on the pressure, the temperature, and the current density, and it encompasses four elements: the reversible cell voltage (the Nernst voltage), the oxygen evolution reaction (OER) charge transfer overpotential at the anode, the hydrogen evolution reaction (HER) charge transfer overpotential at the cathode, and the overall ohmic potential drop in the cell (Figure 2a). The difference within the experimentally observed potential and the value estimated thermodynamically is called the overpotential, and it encompasses all the electrical and the catalytic losses. The ion transport resistance in the layer beside the catalyst activation controls the overpotential cell voltage. The impact of pressure and temperature on the voltage of water electrolysis is displayed in Figure 2b. The rise in temperature increases the reaction kinetic and thus minimize the required voltage. However, the rise in pressure increases the required voltage, but it improves gas management, which is beneficial to the overall efficiency.

The cell voltage is estimated by using the following equation [11]:

$$V_{cell} = \frac{\Delta G}{2F} + \sum_{i=1}^{n} R_i + |\eta_{H2}| + \eta_{O2}\, j \tag{4}$$

where R_i ($\Omega \cdot cm^2$) is the surface resistance of the i^{th} cell element (including ionic and electronic conduction), η_{H2} (in V) is the absolute value of HER overpotential, and η_{O2} (in V) is the OER overpotential. This correlation might be utilized for any value of current density.

- Faradaic efficiency.

There is a mismatch between the amount of hydrogen that can be stocked and the quantity of generated hydrogen. The estimation of the amount of output hydrogen pursuant to the provided power and energy efficiency is performed and presented by Faradaic efficiency. This is expressed as the ratio of the measured quantity of output hydrogen and the theoretical quantity of output hydrogen:

$$\eta_{Faraday} = \frac{V_{H2(generated)}}{V_{cell}(calculated)} \tag{5}$$

An evaluation of the theoretical volume of gas is performed by using Faraday's second law. The estimation of the volume of gas relies on many factors, including the current density, the working surrounding (pressure and temperature), the electrode area, and the electrolysis duration. Water–gas displacement or gas chromatography could be used to evaluate the experimentally developed volume of gas.

Under a low current density, the Faradaic losses are more recognizable, and an increase in hydrogen pressure leads to a lower Faraday efficiency [12]. However, there is no influence of the temperature on Faraday's efficiency [9]. The layer's wideness and the Faraday performance are proportional, and the reduction in layer wideness lowers the Faraday efficiency. This may be attributed to the phenomenon of gas crossover, wherein a part of hydrogen formed at the cathode under unstable high pressure is repelled to the anode, provoking a reduction in Faraday performance.

- Compression effort.

Compression effort is a performance loss induced by a system. The compression process of the produced gas is included in the performance of the system, and it is termed the effort for gas compression ($\eta_{c,H2}$). It is estimated by dividing the work demanded to compress the hydrogen by the quantity of hydrogen that might be stocked while taking into account the mechanical performance of the compressor [13].

$$\eta_{c,H2} = \frac{W_c}{Q_{stored,H2}} \tag{6}$$

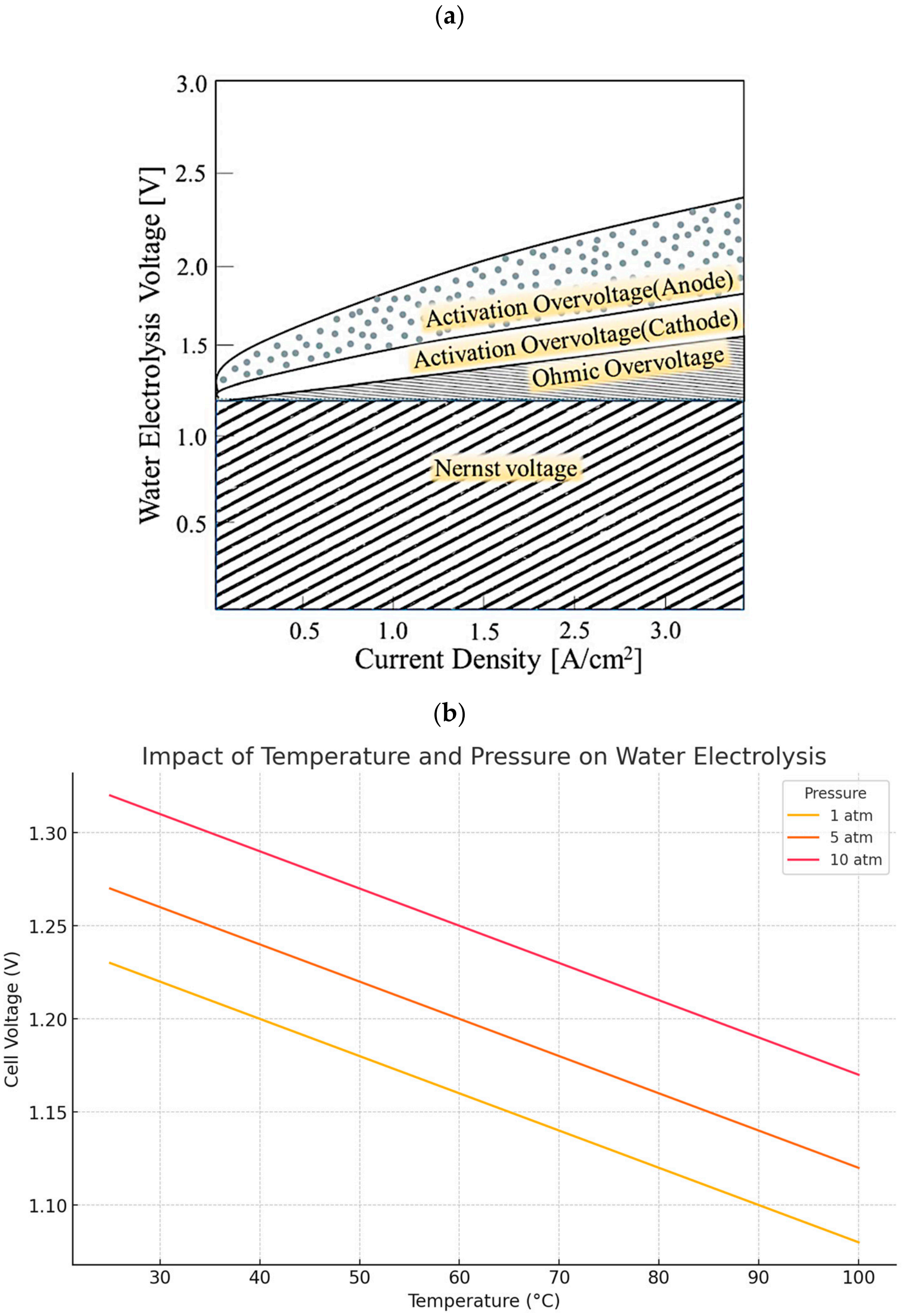


Figure 2. (**a**) I–V characteristic curves of the constituents of water electrolysis [10]; (**b**) Impact of temperature and pressure on water electrolysis**.**

The power demanded for compression is calculated by using the following equation:

$$W_c = n_s W_c^1 \tag{7}$$

where W_c^1 is the needed power for a single compression stage, and n_s is the phase number.

The overall performance of the PEM system relies on the hydrogen performance, the Faradaic performance, and the work performed to compress the hydrogen. It is estimated by using the following equation [14]:

$$\eta_{total,H2} = \eta_{p,H2}\eta_{Faraday}\eta_{c,H2} \tag{8}$$

The total performance of PEMWE is predominately dominated by the hydrogen generation performance, according to Scheepers, Stähler [14].

3. Parameters Influencing the Performance of PEMWE

Several conceptual and functional parameters affect the efficiency of PEMWE, such as the current density, the temperature, the water flow, the pressure at the anode and the cathode sides, the conceptual design of layer, and the catalyst.

3.1. Functional Parameters

3.1.1. Effects of Temperature on the Efficiency of PEMWE

Electrolyzers should be run under high-temperature conditions to achieve a high performance. The working temperature influences the performance of PEM by affecting the reversible voltage and the ohmic and the charge transfer overpotential on the cathode and the anode sides (Figure 3). The rise in temperature minimizes the ohmic overvoltage, the reversible voltage, and the activation overvoltage at the cathode and the anode regions.

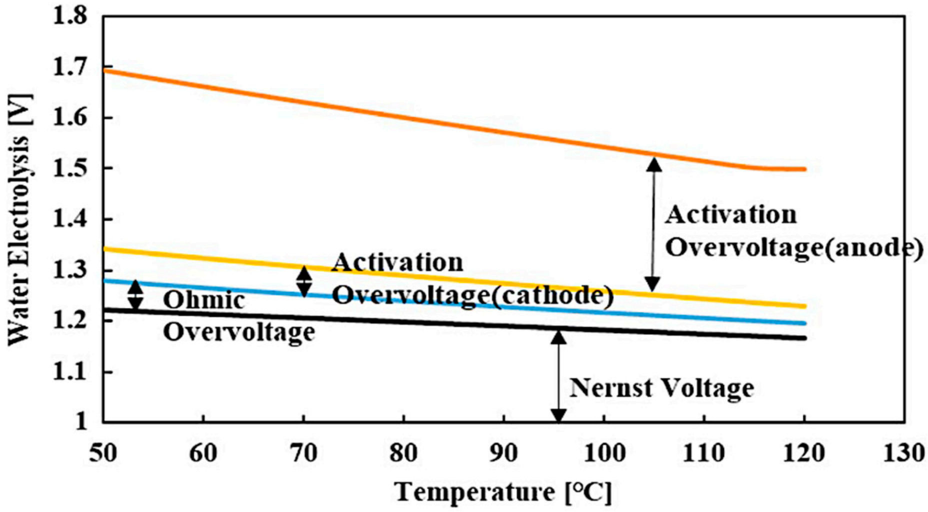


Figure 3. Effect of temperature on PEMWE voltage at 0.8 A/cm^2 and 0.2 MPa and a layer wideness of 60 µm [10].

The reaction rate increases at the electrode with the rise in temperature, leading to a rise in the exchange current density, which reduces the activation overpotential. Several investigations have been conducted to study the influence of temperature on the performance of PEMWE. Ref. [15] investigated the effect of temperature on ion conductibility, the resistance of the polymer electrode, and the working cell voltage with the aid of an evolved model. The simulation results reported a reduction in ohmic resistance from 0.198 Ω/cm^2 to 0.125 Ω/cm^2 with a rise in temperature from 40 °C to 80 °C. Also, a decrease in the operating cell voltage from 2.13 V to 1.98 as the temperature rises from 40 °C to 80 °C under a current density was recorded. In contrast, the working temperature does not influence Faraday's efficiency, according to a study conducted by the authors of [16]. Ref. [17] developed a mathematical model to discuss the leverage of several parameters on the efficiency of PEMWE. The results revealed a decrease in voltage by 8.3% and an enhancement in energy and exergy efficiency by 5.6% and 5.8%, consecutively, as the temperature rises from 313 K to 353 K at a current density of 1.2 A·cm^2. An electrochemical investigation on the leverage of temperature on the efficiency of PEMWE was conducted by the authors of [18]. The results reported that the rise in temperature induces a change of current density under the same MEA conditions and a rise in ionic conductibility has substantial positive leverage on the effectiveness of PEMWE. The ion conductibility recorded an increase from 0.191 S·cm^{-1} to 0.211 S·cm^{-1} as the temperature increased from 75 to 85 °C. In addition, the increase in temperature reduces the activation potential, resulting in an exponential amelioration of efficiency. The authors of [17] conducted a numerical study, based on an evolved CFD model, to study the effect of temperature on the efficiency of PEM under a temperature range of 293–373 K. The results revealed that the rise in working temperature decreases the energy demanded to obtain the same density, contributing to enhancing the PEM effectiveness. This could be interpreted by considering that the rise in temperature enhances ionic conductibility and electrochemical activities. Also, the findings showed that the impact of temperature becomes significant under a high current density (Figure 4).

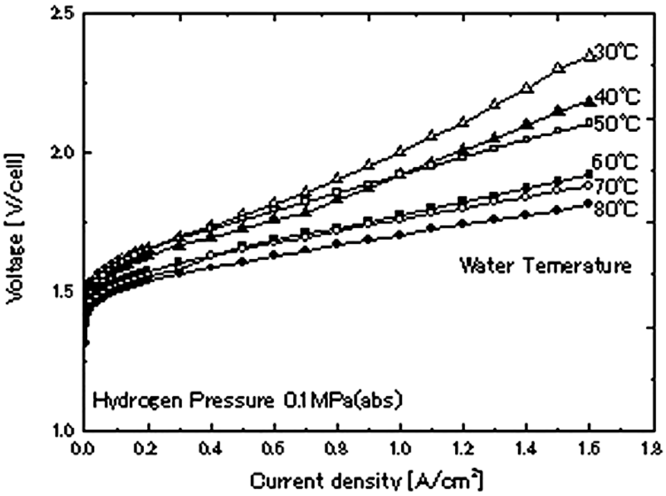


Figure 4. I–V characteristics curve of PEM water electrolysis for various working temperatures [19].

Nevertheless, the improvement in cell performance with the rise in temperature has a limit due to the vaporization of electrolytes at working temperatures passing 100 °C. Since water evaporates at a temperature greater than 373 K, the temperature should not be increased to transcend 373 K, and water is required to be liquified to conserve the ionic conductibility at the electrolyte layer. A rise in temperature above 100 °C leads to minimizing the liquid saturation, as well as water shortage deficiency, which could be prevented through a pressurized operation. In addition, water is required to be purified before using it in PEMWE since unpurified water can degrade the materials and the components of PEMWE. The quality of water is usually specified by the commercial manufacturers regarding conductivity and total organic carbon content. The feasibility of pressurized operation in preventing the reduction in liquid saturation was studied by the authors of [10]. The results reported that the increase in temperature to 120 °C and the pressure to 0.22 MPa restrained the saturation under 0.3 and decreased the overvoltage from 1.57 V to 1.51 V. The rise in temperature above the accepted limit does not only affect the liquid saturation—it can also degrade the layer. The influences of the current density and the temperature on 1D PEMWE, which has been designed to include chemical deterioration, were studied by the authors of [20]. This study was based on measuring the time change in the layer's wideness with the change in the temperature in the situation of a constant current density. The results proved that lowering the membrane wideness below 50% requires a time of 35,000 to 8700 h for an increase in the temperature from 333 K to 353 K. The decrease in the membrane width with the rise in temperature can be explained by the chemical degradation, the mechanical stress and creep, the dehydration, and the water content loss. The rising in temperature can accelerate the degradation of membrane material due to thermal stress, resulting in thinning of the membrane over time. Also, the rise in temperature can induce mechanical stress in the membrane owing to the thermal expansion between the membrane and other components in the electrolyzer, leading to reduced thickness. Additionally, the rise in temperature can cause dehydration of the membrane if the working conditions are not carefully controlled, resulting in a decrease in the membrane's thickness since the polymer structure collapses slightly in the case of insufficient water to maintain its swollen state. The diminution of the layer wideness leads to a hydrogen and oxygen crossover that can cause an explosion. In such circumstances, a cooling system should be combined to maintain the temperature under 373 K, and robust materials are needed. An analysis study conducted by the authors of [14] on the influence of temperature on the effectiveness of PEMWE demonstrated that a low stack temperature has more effect compared to a high temperature. It has been reported that a decrease in the penetrability of gas through the membrane with a decrease in temperature reduces the quantity of hydrogen that permeates via the layer. This is considered as safer per the fact that a rise in the hydrogen volume fraction in the oxygen above 4% leads to a rise in security issues owing to the formation of explosive gases in the oxygen area. Additionally, this study pointed out that the value of the optimal temperature lessens to reach the ambient temperature with low current densities. In addition, there will be no need for durable materials that are required in the case of high temperatures.

3.1.2. Effect of Cathode Pressure on the Effectiveness of PEM

The hydrogen generation rate increases when the cathode operates at higher pressures since high pressures can enhance the mass transfer rates of the reactants and the products across the membrane. Additionally, a reduction in the energy needed for the phase change from liquid to gas owing to higher pressures can shift the vapor–liquid equilibrium of water, resulting in enhancing energy efficiency. Also, the overpotential needed for the hydrogen evolution reaction reduces under higher pressure, leading to an enhancement in the voltage efficiency of the electrolysis process.

Nevertheless, an inverse displacement of H^+ ions from the anode to the cathode is caused by a rise in pressure at the cathode, leading to a rise in over-voltage and decelerating the electrochemical reactions (Figure 5). Consequently, a rise in pressure at the cathode adversely influences the exergy and energy performances of the PEMWE.

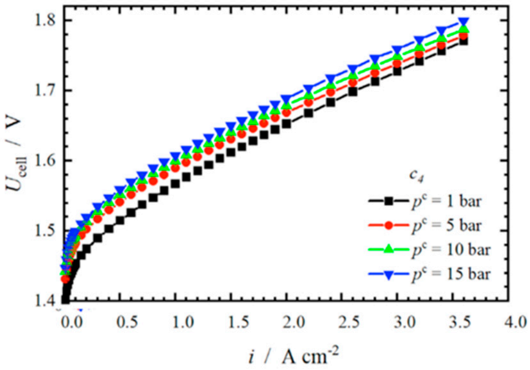


Figure 5. I–V characteristic curve for various cathode pressures [21].

The impact of the pressure change in the cathode area on the efficiency of PEMWE, while retaining the pressure at the anode area at atmospheric pressure, has been investigated by the authors of [22]. The results revealed a decrease in the PEMWE efficiency with a rise in pressure; the leverage of pressure on the augmentation of reversible cell voltage under a high current density is more pronounced than that of lowering on overvoltage, raising the required cell voltage as the cathode pressure rises. Moreover, the input current increases as the pressure increases from 1000 kPa to 2000 kPa. Additionally, a study was carried out by the authors of [17] to analyze the effect of the cathode pressure on the performance of PEM, which revealed that a reduction in cathode pressure from 4 bar to 1 bar leads to minimizing the voltage of PEM by 4.8%. Moreover, as reported by Yodwong, Guilbert [12], the increase in hydrogen pressure decreases the Faraday performance. Even though rising cathode pressure can enhance the efficiency of the electrolysis reaction, the energy required to compress the hydrogen balances out these gains. In terms of stability and safety, rising pressure can add mechanical stress to the system components, negatively affecting their durability and their lifetime. This leads to a rise in capital and maintenance costs due to the need for robust and more durable materials and components. Also, the risk of hydrogen leakage increases, requiring robust safety protocols to manage this risk.

The enhancement of the efficiency of PEMWE by raising the cathode pressure should be carefully assessed against the associated technical and cost challenges. The main focuses of research in the field of cathode pressure are materials sciences and engineering to develop more robust systems that can effectively operate under higher pressure with reduced energy consumption for compression. A PEMWE system constituting a five-cell PEMWE stack able to resist 50 bar and a catalyst-coated proton-exchange membrane to create a membrane electrode assembly was created by the authors of [23]. This developed PEMWE stack can generate a constant scale of hydrogen within the limits of 0 to 50 bar without any deemed variation. A diminution of the contact resistance within the metal bipolar plate and membrane electrode assembly is achieved in this design. Also, the effect of the pressurized gas generated on the efficiency of PEMWE is insignificant. A numerical model based on the Nernst equation was developed by the authors of [24] to evaluate the performance of PEMWE under pressure conditions of 1 and 90 bar and at temperatures of 52 °C and 90 °C. Additionally, the possibility of generating high-pressure hydrogen without the need for a mechanical compressor was demonstrated since there was no deemed change in the cell efficiency owing to the pressure difference.

3.1.3. Impact of Current Density

The current density significantly affects many aspects of the electrolysis process, involving system efficiency, the rate of hydrogen generation, and the lifetime of the system. The rise in current density leads to a rise in the rate of the electrochemical reaction that occurs at the electrode surfaces, improving the rate of hydrogen generation. The permeation of the hydrogen is actively affected by the current density. Ref. [25] reported that a rise in current density to 1 A/cm^2 could raise the hydrogen permeation in a similar way as the rise in the cathode pressure to 20 bar and many decenniums rise in temperature. The rise in the current density induces a reduction in the stack voltage, leading to improved cell performance. This might be attributed to the fact that the rise in current density increases the kinetics reaction on the electrodes, resulting in lessening the charge transfer resistance and thus enhancing cell performance [26].

In contrast, the high current densities produce large amounts of gas, causing a collection of O_2 that can generate two distinct phase flow regimes and protect the anode electrode from water. It should be mentioned that the generated gas mass transport and water could be afflicted by these problems. The accretion of produced gas in PEMWE when the gas generation in the catalyst's region transcends the gas sweep capability of the flow channels causes blister obstruction. The leading reasons for the blister obstruction are the cross-sectional and the water flow rate via the ducts. An investigation study of the behavior of the two-phase flow in the anode flux channel of a PEMWE, with the aid of an optical visualization, was conducted by the authors of [27]. The results revealed that a delay from bubbly to slug transition is provoked by a high water flux rate and leads to creating tinier blisters and reduced slugs. In terms of energy efficiency, the anodic and cathodic overpotentials increase with the rise in current densities, meaning that additional voltage is required to drive the electrochemical reaction at a desired rate, causing in reduction in the energy efficiency. Also, a rise in the ohmic losses is caused by the rise in current density due to the resistance of the electrodes, the electrolytes, and electrical connectors, leading to a further reduction in the overall energy efficiency of the system. A high current density can negatively affect the durability and lifetime of the PEMWE. An acceleration in the degradation of the electrode is caused by the rising current density. The higher flux of ions and higher working temperatures under high current densities generate stress on the membrane, resulting in fast degradation. Additionally, the working temperature plays a significant role in the effect of the water flux on the cell performance. The behaviors of two-phase flow and gas blisters in the anode area of PEMWE, using high-speed optical imaging and under different operating circumstances, were determined by the authors of [28]. The study reported a high efficiency with the anode parallel flow field design in comparison to the single serpentine flow field. Also, the long channel length increases the gas accumulation and the channel blocking, leading to lessening the performance of PEMWE.

Operating a PEMWE under a high current density should consider a balance between efficiency, output, and lifetime. Modern PEMWE incorporates advanced control systems to optimize the current density based on real-time data to balance the lifetime, the output, and the efficiency.

3.1.4. Impact of Flow Rate

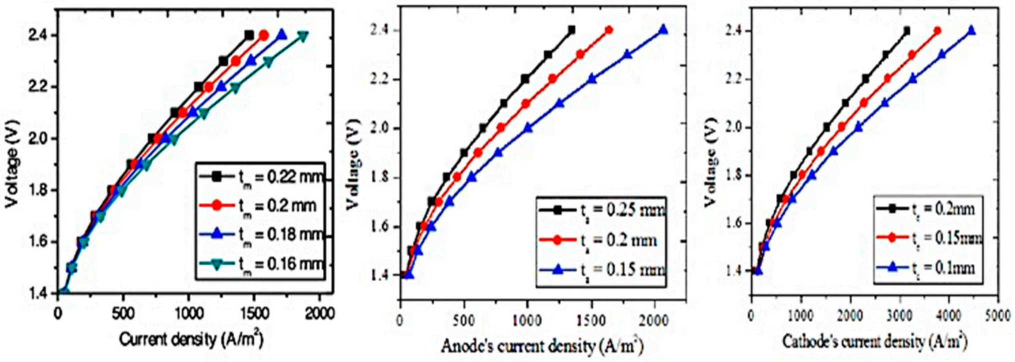
The flow rate is one of the parameters influencing several aspects of a PEMWE's performance. The use of solid polymer membranes to conduct protons and act as obstacles to separate gases in PEMWE can face a change in the efficiency of the management of reactant water and product gases. The increase in the flow rate of water through the electrolyzer can increase the mass transfer of reactant to the reaction sites and the removal of product away from the electrode surface. This can lead to maintaining high reaction rates and minimizing the concentration overpotentials. There is an optimal flow rate that avoids excessive pressure drops or hydraulic losses, which can negatively affect the overall system efficiency. A match between the flow rate and current density should be ensured since a high current density requires a higher flow rate to ensure a sufficient supply of reactants, remove of heat and products, and reduce overpotential. This matching can prevent the buildup of gases that can block the active sites on the electrodes. The impact of the flow rate on the performance of PEMWE by using the magnetic flux density was studied by the authors of [29]. The results showed a rise of 33% in the current density under a flow rate of 300 mL/min, 0.5 T magnetic flux density, and 2.5 V. The magnetic flux density raises the flow rate, which positively affects the performance besides its role in accelerating product outgassing from the electrode surface, resulting in minimizing mass transport losses [30]. In terms of heat management, a higher flow rate can help in removing the heat generated during the electrolysis process. This can positively affect the lifetime of electrolysis since effective heat management is essential to keep optimal membrane and electrode temperatures and avoid overheating. Also, a higher flow rate that can maintain a stable operating temperature can improve the overall electrochemical efficiency. From an operational stability point, proper flow rates can maintain a uniform distribution of reactant through the electrode surface, which is essential for homogenous reaction circumstances, and avoid any hot spots or dry-out conditions in the membrane. Additionally, a reduction in the possibility of gas crossover, which involves the diffusion of hydrogen through the membrane to the oxygen side and vice versa, can be achieved by a high flow rate that can rapidly remove the gases from their respective electrode areas.

3.2. Conceptual Parameters

The layer and electrode wideness and the porosity of the cathode and the anode are conceptual parameters influencing the performance of PEMWE.

3.2.1. The Layer and Electrode Wideness

The layer wideness is regarded as a crucial conceptual parameter influencing the efficiency of PEMWE. The leverage of the layer and the electrode wideness on the effectiveness of PEM was investigated and analyzed by the authors of [31]. The results reported a decrease in the performance of PEMWE with the rise in layer wideness (Figure 6a) because the ionic and electric resistance boost with the extension of the layer wideness and lead to lower voltage, thus increasing ohmic loss. Additionally, the rise in the anode gas diffusion layer‘s wideness and the cathode gas diffusion layer‘s wideness reduce the voltage (Figure 6b,c), and the high current densities cause a significant reduction in the voltage. The rise in the layer wideness entails a rise in the ohmic resistance and raises the needed power [22]. In addition, the high current density intensifies the impact of layer wideness on the voltage. The Faraday performance diminishes with the reduction in membrane wideness, and the effect is more prominent at a high cathode pressure. This is attributed to the reduction in the hydrogen’s flux densities through the membrane and output rates when the layer wideness decreases, contributing to a lower Faraday performance.



(**a**) (**b**) (**c**)

Figure 6. Impact on the efficiency of (**a**) the layer wideness, (**b**) the anode GDL’s wideness of GDL, and (**c**) the cathode GDL’s wideness of GDL [31].

Ref. [17] conducted a parametric study to analyze the impact of layer wideness and the channel dimensions on the voltage, exergy, and energy efficiencies of PEMWE. The results reported a decrease in voltage and a rise in energy and exergy efficiencies with a decrease in layer wideness and dimensions of the channel. The rise in the width and the height of the channel augment the ohmic resistance and the electrolyzer’s voltage. The cross-sectional area increases with the rise in the width and the height of the channel, provoking a reduction in the water velocity and reaction rate and a rise in cell voltage. Consequently, a reduction in the layer wideness is needed to minimize the ohmic resistance, the needed power, and the price. However, an immoderation diminution of the layer wideness might negatively influence its endurance and result in a penetration of the reactive gases.

3.2.2. The Porosity of Cathode and Anode

The porosities of the cathode and the anode influence the efficiency of PEMWE. A study was conducted by the authors of [31] to analyze this effect by changing the porosity of one electrode while maintaining the porosity of the second electrode constant. The results are displayed in Figure 7 and reported an improvement in PEMWE with the rise in porosity at a high voltage, and this effect is important for the cathode. This can be interpreted by the electric resistance that is low at a high porosity since it has a low volume fraction. In addition, the diffusion loss diminishes as the porosity rises, contributing to enhancing the PEMWE performance. Rising porosity in both the anode and the cathode allows better gas diffusion and mass transport, leading to easier access of the reactants (water at the anode and hydrogen ions at the cathode) to the reaction sites, and the output products, oxygen, and hydrogen, can be easily removed. Additionally, the rise in the porosity increases the electrochemical surface area, leading to a rise in the number of active sites for the electrochemical reaction, resulting in enhancing the efficiency of PEMWE. However, the rise in the porosity above the optimal range negatively affects the mechanical stability and minimizes the contact between the catalyst and the membrane, causing lower efficiency.

The rise in porosity at the anode side ensures a better water distribution, ensuring hydration of the membrane, which is fundamental for proton conductivity. On the other hand, the rise in the porosity at the cathode side helps in the removal of the hydrogen gas, resulting in efficient gas removal and thus preventing flooding, which negatively affects efficiency.

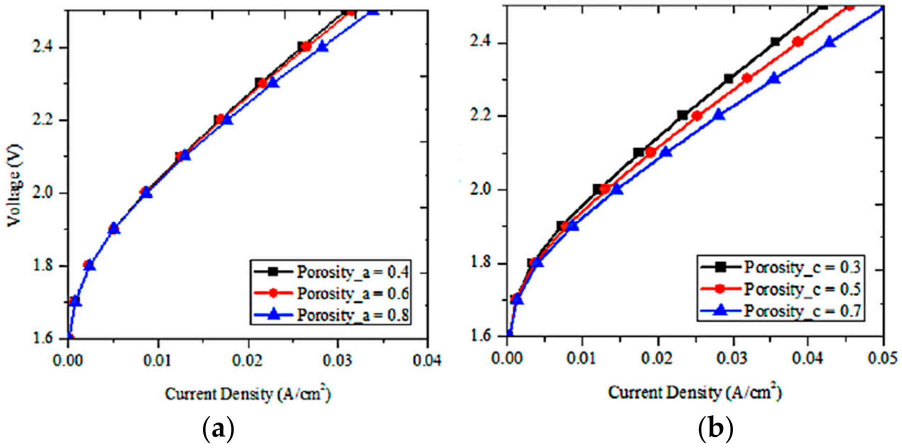


Figure 7. Impact on the PEMWE efficiency of (**a**) porosity of anode and (**b**) porosity of cathode [31].

3.2.3. Gas Diffusion Layers (GDLs)

GDLs are one of the components of PEM that sandwich the MEA from both parts. They are used to conduct the electrons between the cathode and the anode, to transport the water into the MEA, and to transfer the gases from the catalyst layer toward the MEA. Thus, proper design of the GDL is needed to ensure an even distribution of water to enhance the reaction site and increase efficiency. Additionally, a proper design is required to ensure quick transportation of the gases away from the reaction sites to avoid gas bubble accumulation, which can block the active sites and hinder the electrochemical reactions. In terms of electrical conductivity, GDLs facilitate the conduction of electrons between the catalyst layer and the current collector, requiring high electrical conductivity because poor conductivity can increase energy losses and reduce the efficiency of the electrolysis. Regarding mechanical support, GDLs provide mechanical support to the membrane and the catalyst layers, maintaining a uniform pressure across the MEA and proper contact between layers, which leads to enhancing ion and electron transport.

The materials of a GDL play an important role in its performance in terms of porosity and hydrophobicity. An enhancement in gas diffusion can be achieved by a highly porous GDL but may block water distribution. Thus, the application of a hydrophobic treatment could ensure efficient water drainage and reserve access to reactant gases. Regarding the materials' thickness, better mechanical support and water retention could be accomplished by a thicker GDL, but this raises the resistance to gas diffusion. On the contrary, a thinner GDL enhances gas transport but may minimize the overall structural integrality and water distribution. A GDL used in PEM is based on carbon materials like carbon cloth or carbon paper. Carbon-based materials have several issues related to their high sensitivity to be oxidized at the anode side with potency in releasing CO_2 because of the high oxygen revolution reaction at the anode [32]. Metallic-based GDLs are viewed as a suitable candidate thanks to their high mechanical robustness and conductibility. Porous titanium mesh and felt have the benefit of corrosion resistance in an acidic environment, making them an ideal option for an anode GDL [33,34]. However, during operation, the impedance of titanium GDL rises because of the creation of a TiO_2 passivation layer, which raises the connection impedance within the GDL and the other elements of PEM [35]. Coating GDLs with Pt or IrO_2 layers is one of the existing options to reduce this effect. However, this raises the cost of GDLs, and consequently, the cost of the PEM electrolyzer will be higher [36].

GDLs play a significant role in managing the phase flow of liquid water and gaseous products in the system by enabling water to reach the catalyst layer and concurrently remove the generated gas. Thus, a suitable GDL could prevent flowing or drying issues related to poor water and gas management. Additionally, the structure of the GDL affects the formation of gas bubbles and their discharge from the catalyst layer. A performant removal of gas is crucial to avoid bubble accumulation that raises mass transport resistance and minimizes the efficiency of PEMWE.

Uniform contact between the GDL and MEA should be applied to prevent an irregular current distribution that leads to a rise in the degradation of the layer. Titanium is made of sintering titanium particles with a rough surface and weak contact. Microporous layers of Ti are based on depositing smaller particles of Ti on Ti GDL and are used to enhance the connection between GDL and the MEA and control the porosity of Ti GDL, which affects the mass transport of water and O_2 and H_2 generated at MEA.

The GDL requires special exigencies like corrosion impedance, with high conductibility and low mass transfer losses [37]. The mass transfer impedance and interaction impedance between the MEA and the GDL depend on the porosity, the composition, and the wideness of the GDL [38]. Optimization of the titanium current collector by conglomerating Ti particles with changing the size was performed and analyzed by the authors of [39]. The results reported that the optimum particle size was 50–75 µm with a pore size of 12–13 µm. An antimony-doped tin oxide (ATO) blended with a Nafion solution over the titanium felt was used and studied by the authors of [33]. The results revealed an improvement in the electrolyzer activity in the voltage range influenced by the charge transfer kinetics.

The GDL has a considerable effect on the efficiency of PEMWE. The GDL can reduce losses and raise the overall efficiency by ensuring efficient reactant delivery, electrical conductivity, and gas removal. Thus, proper design and optimization of GDLs are crucial to enhancing the performance of PEMWE.

3.2.4. Bipolar Plates (BPs)

Bipolar plates offer many functions, such as heat transfer, retaining the separation between O_2 and H_2 in the cell, mass transport, and ensuring structural stability for electrolyzer systems operating at high pressure [40]. BPs serve as conductive paths, allowing the transfer of electrical current between the adjacent cells in the PEM electrolyzer stack. Thus, a higher electrical conductivity material is crucial to reduce the ohmic losses and the energy losses and rise the efficiency. Additionally, BPs contain a flow channel that is designed to direct the water to the catalyst layer and remove the gases. Thus, the flow field should be well designed to ensure an even water distribution, which is essential to maintain efficient reaction kinetics. Moreover, the design of the flow channel should consider the reduction in the pressure drop and maintain sufficient water and gas flow because a high pressure drop leads to a rise in the needed energy to pump water through the system, resulting in decreasing the system efficiency.

In terms of thermal management, BPs could manage the distribution of heat generated by the electrochemical reaction, according to the cell. Poor heat management leads to the formation of local hotspots, which damage the membrane and minimize efficiency. Thus, BPs with good thermal conductivity are essential to facilitate heat dissipation and ensure stable and performant operation. In some designs, BPs could involve cooling channels. A suitable integration of the channels is essential for efficient heat management, resulting in enhancing the overall efficiency and longevity of the system.

Bipolar plates are exposed to harsh working conditions, such as high acidity and oxidation potential on the anode sides. Thus, the BPs at the anode side should be invulnerable to the oxidizing medium because the oxidation at the anode provokes the oxidation of metallic BPs. Corrosion can degrade the materials, resulting in a gradual rise in the electrical resistance and the release ability of the metallic ions that can poison the catalyst or membrane. Additionally, corrosion of BPs leads to contamination of the PEMWE by the released ions, resulting in lower electrochemical performance. At the cathode area, the corrosion of BPs is less compared to the anode area, while the absorption of hydrogen on the metal causes hydrogen embrittlement [41]. Many approaches have been discussed in the literature to minimize the passivation and the resistance of the materials used in BPs through the deposition of metal oxide films and noble metal sheets, such as titanium-based BPs and stainless steel BPs, which are presented below.

- Titanium-based BPs: Titanium-based bipolar plates are oxidized owing to the high oxidizing medium and form a TiO_2 layer that has a low electrical conductibility, resulting in the rising intersectional contact impedance between BPs and the gas diffusion layer. Many investigation studies have been conducted to avoid the passivation of the BPs by coating them with noble metals like Ta_2O_5, Pt, and Au. The coating methods used in the literature are vapor phase deposition, electrodeposition, and sputtering. Titanium coated with Pt is usually used, but it increases the cost of PEMWE. TiN-based coating is one of the options used to coat Ti-BPs via plasma and thermal methods. According to a study conducted by the authors of [42] on the effect of TiO_2 deposits on the TiN coating, the operation of oxidation of the TiN coating is long, and H_2 embrittlement is reduced, which could also minimize the capability of Ti uptake owing to the TiH figuration. The electrodeposition of platinum on Ti-based BPs is an option used to reduce the cost of the coating technique. It minimizes corrosion and oxidation and decreases the ohmic resistance. The authors of [43] proved that the electrodeposition of platinum on Ti-BPs could enhance the performance of electrolysis. Vacuum sputtering is also used to manufacture gold-coated Ti BPs. The advantage of the gold coating is its capability to reduce the creation of a passive layer on the surface. The ideal gold loading to achieve stable electrolysis efficiency is 1 µm [44]. A coating film formed of Ag nanoparticles and TiN applied on Ti BPs showed high corrosion resistance at high potential and in an oxidation medium due to the high electroconduction of Ag and the corrosion-resistant characteristic of TiN.
- Stainless steel BPs: Stainless steel is used as material for BPs thanks to its low price, simpler machining, and less vulnerability to hydrogen embrittlement [45]. However, stainless steel has low corrosion resistance compared to titanium under electrolysis circumstances. For the purpose of protecting BPs from passivation, a dense titanium coating is placed on the stainless steel BPs through the vacuum plasma-spraying process, and a thin film of platinum is placed on the Ti by using the plasma vapor-deposition process. This coating proved to provide good protection of the stainless steel area against corrosion. The optimal wideness to minimize the wideness of the layer and the price of the total stack is 30 µm [46]. A coating of Au/Ti was also tested by depositing Ti using vacuum thermal spraying with electrodeposition of Au. The results showed a reduction in interfacial contact resistance, and the steepness of Ti ensures good cohesion to the electrodeposited Au nanoparticles. The coating was examined in a simulated mash that imitated the PEMWE anode medium [47]. The results revealed long-term protection on stainless steel BPs. RuO_2 was used and located on the ferric stainless steel-based BPs by using the electrodeposition technique [48]. The interfacial contact resistance (ICR) measurement was used and proved to have a positive impact on the deposition of RuO_2 on stainless steel and led to lower interfacial contact resistance. An assessment study of cheap material that could be used for BPs, including stainless steels (SS316L, SS321, and SS904L), was conducted by the authors of [49]. Coating layers of Ti, CrN/TiN, TiN, and Ti/TiN on stainless steel BPs was performed by using the physical vapor technique. For the purpose of determining the best substrate/coating compound for BPs, a corrosion test was used in anodic PEMWE circumstances. In addition, the ICR was measured following the corrosion test. The results revealed that Ti/TiN multi-layered coating on SS 321 recorded the best efficiency with -0.02% weight loss and an ICR of 9.9 $m\Omega$ cm^2 after the corrosion test.

3.3. Impacts of Catalysts

The catalyst is deemed as a significant parameter influencing the efficiency of PMEWE. Enhancing the catalyst's activity leads to reducing the activation overpotential, especially on the anode side. This leads to minimizing the energy needed for water splitting, resulting in a direct reduction in energy cost per unit of hydrogen generated. In the activation part of the polarization curve, the factors that determine the efficiency of PEMWE are the kind of catalyst and the loading, the stability of the catalyst, and the electrochemical active area. The electrocatalysts utilized in PEMWE are usually noble metal-based, like RuO_2/IrO_2 catalysts as an anode for the oxygen evolution reaction (OER) and Pt/Pd-based catalysts for the hydrogen evolution reaction (HER) [50,51]. The drawback of these metals is the high cost, resulting in raising the price of PEMWE. Moreover, the price of precursor salt needed in the initial coating process leads to a higher price of PEMWE. Several investigations have been performed to create alternative and cheaper electrocatalysts for HER and OER.

3.3.1. Hydrogen Evolution Reaction Catalysts

HER catalysts on the cathode side should effectively facilitate the diminishment of the proton to the hydrogen at low overpotentials since raising the overall system efficiency and decreasing the energy consumption are achieved by higher activity and a lower overpotential. The hydrogen evolution reaction has electrocatalyst activity that relies on the strength of the Me-H bond. The plot 'Volcano' presents the relation between the strength of Me-H and the current density of the HER [52]. It may be viewed in Figure 8 that the highest HER efficiency can be achieved through noble metals since they have hydrogen-binding energy within reach of the optimum, leading to making the thermodynamic transition from reactants to products easier.

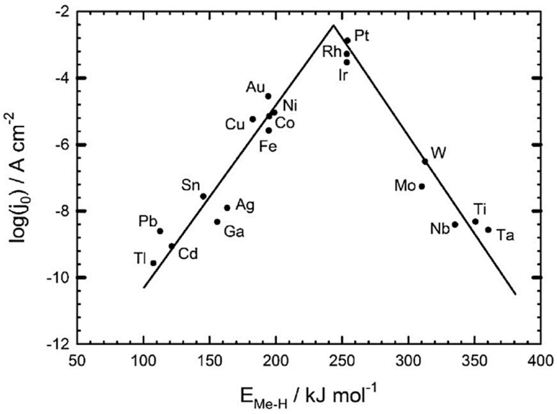


Figure 8. Volcano plot to express the correlation between the exchange current density and the Me-H bond strength [52].

Platinum-group noble metals are regarded as the most active candidates to be used as catalysts in the HER. Despite the high catalytic effectiveness of the Pt, their scarcity and high cost make them inconvenient to be used in large industrial applications [53]. Many investigations have been conducted to optimize the geometric parameters of Pt-based catalysts by reducing the noble metal quantity while keeping electrocyclic activity. Backing platinum nanoparticles on a high-surface carbon is a cheap and easy approach to making active electrocatalysts. The most frequently used method is 20 wt% Pt placed on carbon black (Pt/C), and it could accomplish one of the smallest values of overpotential of 46 mV under 10 mA/cm^2 [54,55]. The atomic layer deposition (ALD) technique is also one of the options utilized to lessen the use of precious metals. It is based on the elaboration of Pt nanoparticles, monolayers, and nanoclusters of an accurately controlled size [56,57]. This technique could significantly minimize the quantities of noble metal (up to 1/10th of a standard Pt loading of approximately 300 $\mu g\ cm^2$) [58].

Many studies have been conducted to find a cheaper alternative electrocatalyst to noble metals such as MoS_2, Palladium, and non-precious metals. The feasibility of using an MoS_2 electrocatalyst in the HER was tested by the authors of [59]. The results demonstrated that the MoS_2 might be utilized as an electrocatalyst in the HER. The incorporation of MoS_2

with RuS_2 was suggested by the authors of [60] to be used as a catalyst, and the results reported excellent output of this combination, like a satisfactory overpotential and Volmer Tafel behavior and high exchange current density. The benefit of this combination is the ability to enhance hydrogen production to attain 1.2 L/h under an operated current density of 1 A/cm^2, a power of 41.8 W, energy utilization of 3.8 kWh/Nm^3, and a performance of 93%. Palladium is regarded as another nominee for electrocatalyst thanks to its remarkably electrocatalytic effectiveness and its reduced cost compared to platinum, and it is presented in abundance on Earth [61]. The utilization of carbon-supported electrocatalysts, such as Ni_2P/CNTs, Mo_2C/CNTs, A-Ni-C, WO_2/C nano-wires, Co-doped FeS_2/CNTs, and CoFe nanoalloys embedded in N-doped graphene, have been enormous in studies to examine and assess their abilities to substitute Pt in HER and lower the price of catalysts utilized in HER [62–66]. In addition, many studies have been performed to investigate the utilization of alternative catalysts to Pt-based catalysts for HER in-PEM electrolysis. The findings showed that the catalysts MoSx and Pd-based nanocarbon are the best electrocatalysts in terms of electrocatalytic effectiveness and endurance. Palladium catalysts have an electronic configuration identical to Pt and are also used as alternative catalysts to enhance the performance of PEMWE, owing to their good catalytic activity for hydrogen-oxidation and oxygen-reduction reactions, as well as their excellent stability and durability under acidic conditions. Also, they are cheaper than Pt, reducing the overall cost of the catalyst. Pd could achieve a high electrochemically active surface area when it is loaded on carbon powders or other novel supports, including a carbon nanotube and graphene [67]. Additionally, the nature of the support materials significantly affects the catalytic activity of Pd catalysts, in which the performance of nanostructures is better than that of the particles [68]. The adjustment of the electronic structure that could affect the catalytic activity of the Pd catalyst can be achieved by using Pd with other metals. Studies showed that alloying Pd with non-noble metals could enhance performance and stability in addition to minimizing cost [69]. Recently, the use of non-precious metals, their compounds, and their use as catalysts in HER have received significant attention and progress. The main factors influencing the catalytic effectiveness are the auspicious harmonious effect between different metals, the anion/cations relation, the kind of catalyst support with a high geometric design, and the core architecture of the nominated catalyst. Minimizing the use of precious metal by alloying it with cheaper metals is a successful approach and has been used. The use of one or more metals to further benefit the catalytic effectiveness of the precious metal is an excellent method. The authors of [70] conducted a study to examine the use of cheap metal, Co, Ru, Au, Fe, and Cu, with Pt. The results demonstrated the feasibility of using these metals and presented the reasons behind the improvement in their performances compared to Pt nanoparticle-based catalysts. A 'lattice strain effect' affects the surface Pt-Pt bond gap by reason of introducing another metal [71]. A 'ligand effect' is attributed to the variation of the electronic features of the active areas of one transition metal by inserting different metals [72]. Even though the approach could reduce the cost of catalysts while maintaining cell efficiency, the rarity and the price of the precious metals are still deemed as dominant barriers to mass extension in manufacturing.

The support material and the available catalytic area, in addition to the convenient materials used as an electrocatalyst, play a significant role in the performance of HER. The rise in surface area leads to an improvement in the reaction rate, resulting in enhancing the hydrogen production rate.

3.3.2. Oxygen Evolution Reaction Catalyst

The oxygen evolution reaction comprises four electrons with a bigger overpotential compared to HER. However, the kinetic of HER is quicker compared to OER. The OER in PEM occurs in an acidic condition and needs a catalyst to be effective and stable under corrosive circumstances. The loading needs of the OER catalyst should be minimized while attaining high activity to minimize the overall cost of PEMWE. Many transition metals, involving noble and non-noble materials, have been studied and tested to be used as electrocatalysts in OER. The materials used as electrocatalysts should be able to withstand the corrosive oxidative environment at the anode and should have relatively good catalytic activity. The two metal oxides IrO_2 and RuO_2 have shown better metallic conductibility among the metal oxides [73]. Iridium offers a good balance between activity and stability owing to its inherent characteristics, allowing it to be a suitable candidate as an electrocatalyst in OER. However, its use faces a challenge due to its high cost and rarity. RuO_2 has proved better effectiveness for OER and more effective than IrO_2 but is unstable by reason of corrosion induced by the high acidity of the perfluoro-sulfonic layer and the high anodic potential at OER [50]. Nevertheless, IrO_2 recorded a larger impendence to PER in an acidic environment and poor performance [74].

Several investigations have been carried out to evolve approaches and alternate catalysts for the OER with high stability and function and cheaper cost in reducing the use of Ir. The developed approaches are nanostructuring of Ir, fixing Ir on the supporting substrates, and combining Ir with hetero metals. The nanostructuring of Ir is based on depositing a thin layer of Ir with a low amount on the GDL, and it proved its ability to reduce the use of catalysts while maintaining high activity [75]. Electrodeposition technology is viewed as an efficient technology to assemble a catalyst on the GDL since it can lessen the quantity of the catalyst due to good scattering of the catalyst. In addition, it has been utilized to place IrO_2 on various substrates, like gold, titanium, and carbon paper. A unique catalyst formed of nano-porous Ir nanosheets was suggested by the authors of [76] via alloying Ni with Ir in the shape of a thin film and de-alloying in an acidic environment. This combination provided a significantly improved performance compared to a commercial IrO_2 nanoparticle catalyst. Fixing Ir on the supporting substrates is one of the approaches used to lower the quantity of noble metal used in the catalyst. This approach offers several benefits, such as raising the active surface of the catalyst, boosting the electrical conductibility via strong interconnection between the fixed materials and the supporting, steadying the active species, and avoiding grave accumulation. Ref. [77] tested the use of boron carbide (B_4C) as a supporting substrate for Ir and demonstrated its high effectiveness and endurance for OER. Compared to carbon materials, B_4C has important electrochemical stability besides its high electrical conductibility. Tungsten oxide nanorod was also examined to be used as a supporting substrate for defective thin Ir sheets by the authors of [78]. A hydrothermal reaction was used to prepare an ordered array of tungsten oxide and then deposit Ir on the surface through an electrodeposition process to form nanorods. The results showed a reduction in the mass transport and the total loading of Ir (0.14 mg Ir/cm^2) during the functioning of PEMWE. Moreover, TiO_2 proved its ability to be a good candidate as a supporting material for Ir thanks to its low price, high stability, and availability [79]. A physical mixing of IrO_2 catalyst with a Ti metal support was prepared and tested by the authors of [51]. The results showed that a rise in the scattering of IrO_2 over Ti particles was achieved with high activity when it is employed as an anode in PEMWE.

Alloying Ir with a hetero metal (M, Ni, Cu, Co, and Fe) could optimize the surface chemical characteristics due to the change of charge distributions, with morphological benefits and electronic structure adjustment. The core–shell structure is effective in obtaining an adequate match between effectivity and the constancy of electrocatalysts in PEMWE. The authors of [80] developed a self-building RuO2@IrOx core–shell nanostructure in the purpose of attaining high stability and activity. The self-assembled RuO2@IrOx showed a lower overpotential of 215 mV at 10 mA/cm^2 compared to RuO_2 (260 mV at 10 mA/cm^2) and IrO_2 (316 mV at 10 mA/cm^2). Moreover, this designed core–shell proved to have good stability at 1 A/cm^2 owing to the efficient protection supplied by the IrO_2 shell.

In addition to the material choices, the stability of OER catalysts under functional conditions is fundamental. The stability is affected by the degradation of the catalysts by processes including surface oxidation state changes, dissolution, and particle agglomeration, which can considerably minimize the lifetime and the efficiency of the electrolyzer.

The structure of the catalyst particles, including the size and distribution, has a significant effect on the available surface area for the electrochemical reactions and thus directly affects the mass transfer [81,82]. In terms of size, catalysts with smaller particles offer a larger surface area for chemical reaction, leading to an increase in the number of reaction sites and thus enhancing the use of catalysts. Despite this, a smaller particle catalyst can cause denser packing, leading to a decrease in porosity and blocking mass transfer. Regarding the distribution, a uniform distribution is essential to ensure the complete access of reactants on all parts of the catalyst layer. Thus, this reduces the dead spots where reactions occur, decreasing the gradients and overpotential and enhancing the overall efficiency of the PEMWE.

4. Conclusions

The PEM electrolyzer is regarded as an efficient technology to produce green hydrogen thanks to its various benefits. Nevertheless, the high price, the reduced endurance, the acidic corrosive environment, and the requirement of a high quantity of purified water are the main disadvantages of PEM. The current paper presented the efficiency of an electrolyzer that entails the hydrogen production efficiency, the Faradaic efficiency, and the effort power to compress the output hydrogen. The hydrogen generation efficiency is the highest. Several operating and conceptual factors influence the efficiency of PEMWE, like the catalyst, the temperature, the current density, the cathode pressure, and the layer wideness. The effect of these factors is reviewed and discussed in this paper.

Enhancing the performance of PEMWE can be achieved by optimizing its operating circumstances. Operating the PEMWR under high temperatures raises the quantity of hydrogen produced by minimizing the overvoltage, while it can decay the layer and lessen the lifespan of the PEMWE.

Increasing the cathode pressure minimizes the quantity of power demanded to compress the hydrogen to stock it and thus decreases the cost of generated hydrogen. In contrast, this increase negatively affects the efficiency of PEMWE. Thus, the pressure should be adapted according to the features of the layer. Also, for the purpose of avoiding explosion, the density of the oxygen in the hydrogen should be examined.

The rise in the current density improves the efficiency of PEM electrolysis, while the high current density causes a blister obstruction and two phase-flow, which decrease the effectiveness of the PEM electrolysis.

The design of the gas diffusion layer, which is an essential element of PEMWE, affects the effectiveness of PEMWE. Several methods and designs of GDL have been developed and showed an enhancement in the performance of PEMWE. The decrease in the cost of PEMWE, besides improving its stability, requires the use of a cheap and low-corrosion-resistant GDL. MPL at a micron size is one of the designs that raises the contact between the layer and the GDL. The electrodeposition of a catalyst on GDL proved its ability to enhance catalyst distribution and reduce the corrosion of GDL. Pore-graded GDL at the catalyst layer with the current collector is an effective approach to enhance catalyst distribution on the GDL and prevent catalyst loss, owing to the lading of big pores in foam-based GDL. Also, a thin, tunable GDL design could optimize the ohmic contact and enhance the overall efficiency of PEMWE. Designing a GDL with a very low wideness while maintaining the same or better mass transport, electrical, and corrosion-resistant properties requires more development and research.

The reduction in the layer wideness can improve the PEMWE. However, an excessive decrease in the layer wideness affects its endurance and leads to the permeation of reactive gases. The intensity of the influence of the layer wideness, the cathode pressure, and the temperature on the PEMWE efficiency rely on the current density. The increases in the cathode and the anode porosity boost the PEMWE efficiency at a high voltage, and this effect is more pronounced for the cathode.

The catalyst plays a considerable role in enhancing the PEMWE performance. The catalysts used in the OER and the HER are noble metals, which are costly, resulting in raising the cost of PEMWE. Several alternative cheaper catalysts have been created and proved to have as high power as cheap electrocatalysts. In the OER, an iridium-based catalyst was used as an anode catalyst thanks to its high stability and competent activity. Several studies have been conducted to enhance the robustness and decrease the loading mass of Ir to minimize the cost of PEMWE. The developed and suggested methods are nanostructuring, deposition on conductive substrates, and alloying with hetero metals. The deposition of Ir on a conductive substrate improves the active surface species and boosts the conductibility of the catalyst. The alloying of Ir makes the iridium exist in different oxidation states and reduces the binding energy of oxygen intermediates on the surface. More research is required to improve the alloyed and supported catalyst and to develop more design approaches to ameliorate the catalytic effectiveness of OER-like trimetallic catalytic systems.

Author Contributions: All work was performed by G.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The author declares no conflicts of interest.

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