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Review Article

Comparative Overview of Water Splitting and Biological Techniques of Hydrogen Production

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Abstract

Hydrogen is widely regarded as a cornerstone of the global transition toward low-carbon and sustainable energy systems. However, the environmental benefits of hydrogen depend strongly on the production pathway employed. This review presents a comparative analysis of water-splitting technologies and biological methods for green hydrogen production, highlighting their operating principles, efficiencies, costs, technological readiness, and prospects. Water splitting approaches include electrolytic methods alkaline water electrolysis (AWE), proton exchange membrane (PEM), anion exchange membrane (AEM), and solid oxide electrolysis (SOEC) as well as photocatalytic and photoelectrochemical (PEC) systems. Among these, AWE and PEM are technologically mature and commercially deployed, offering high hydrogen purity and system reliability, while SOEC demonstrates superior thermodynamic efficiency at elevated temperatures. Photocatalytic and PEC techniques provide direct solar-to-hydrogen conversion but remain limited by low efficiencies, charge recombination, and material instability. Biological hydrogen production routes like biophotolysis, fermentation, gasification, and pyrolysis utilize biomass and organic waste as feedstocks, supporting circular economy principles. Gasification and pyrolysis exhibit relatively high hydrogen yields and industrial potential but require high temperatures and extensive gas cleaning. In contrast, biophotolysis and fermentation operate under mild conditions and are environmentally benign but are constrained by low production rates, oxygen sensitivity, and process instability. A critical comparison indicates that electrolytic water splitting currently offers the most viable pathway for large-scale, high-purity hydrogen production when powered by renewable electricity, whereas biological methods present attractive waste-to-energy solutions with lower technological readiness in some cases. Future development should focus on reducing capital costs, replacing precious metal catalysts, improving membrane durability, enhancing photocatalyst stability, and optimizing bioreactor performance. Integrating these advances with renewable energy systems will be essential for achieving scalable, cost-effective, and truly sustainable hydrogen production.

Keywords

Hydrogen, Water Splitting, Electrolysis

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1. Introduction

Climate change has for a long time been linked to anthropogenic activities, activities like energy generation and consumption from fossil sources. These energy related activities have been linked to the contributions of large tons of greenhouse gasses [1].

Recently, the use of hydrogen as a renewable energy source has further sparked the question about the environmentally friendliness of the various methods used in the production of hydrogen even when the product of its usage is harmless water. Till date about 50% of world's hydrogen supply is through steam reforming, 30% through oil and naphtha reforming, 18% from gasification of coal, 3.9% from electrolysis and 0.1% from other sources [2]. Part of the reasons of why hydrogen is posed to be a key player in the long energy transition includes; it's very low Environmental impact factor (EIF), very high Hydrogen content factor (HCF) and very high Greanization factor (GF) in comparison to other forms of fuels [3].

$$EIF=\frac{\text{Kg } CO_2 \text{ product of combustion}}{\text{Kg of fuel}} \quad (1)$$

$$GIF=\frac{EIF_{max}-EIF}{EIF_{max}} \quad (2)$$

$$HCF=\frac{\text{Kg of } H_2 \text{ in fuel}}{\text{Kg of fuel}} \quad (3)$$

To achieve a net zero emissions by 2050, there is urgent need for scaling up of clean and sustainable hydrogen production methods and infrastructure. Achieving this needs substantial advancements in science and technology, investment in green hydrogen production methods, and a clear strategy to integrate hydrogen into various sectors of the economy. This expansion is essential not only to meet future energy demands but also to drive progress towards a sustainable and decarbonized global energy system.

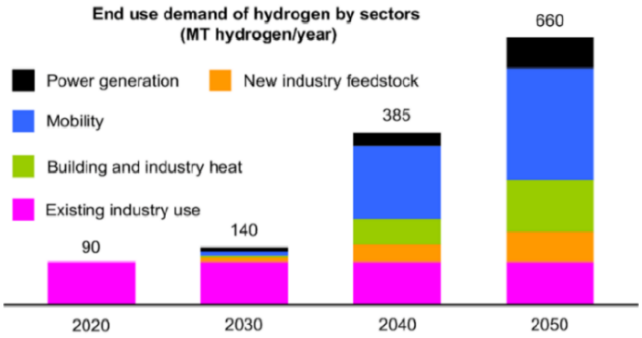

Figure 1. *Projected role of hydrogen towards an emission free energy system by 2050 [4].*

Hydrogen till date is produced largely from fossil base sources like coal, natural gas and oil with China topping in the ranks in both production and consumption of hydrogen. [5].

This paper aims to review water splitting and biological technologies of producing hydrogen which are considered green and sustainable pathways of producing hydrogen. Challenges and future research outlooks will be pointed out with a clear vision of improving these technologies for efficient hydrogen production.

2. Water Splitting

Water splitting can be highlighted as the process of water decomposition into hydrogen and oxygen when it's supplied with sufficient energy greater or equal to its bond energy. Over the years, three (3) water splitting technologies have been on the map of researchers, these technologies include: Photovoltaic-electrochemical water splitting; Photocatalytic Water splitting; and Photoelectrochemical Water.

Regardless of which technology is employed, water splitting's fundamental principle comprises of two half-cell reactions which include: water oxidation reaction also called oxygen evolution reaction (OER) and the water reduction reaction also referred to as the hydrogen evolution reaction (HER) [6]. These reactions of Cathodic (HER) and Anodic (OER) are largely dependent on the pH of the solution or medium. When the medium is Basic the cathodic and anodic reactions are as follows:

$$\text{Cathodic Reaction: } 2H_2O_{(l)}+2e^- \rightarrow H_{2(g)}+2OH_{(aq)}^- \quad (4)$$

$$\text{Anodic Reaction: } 2OH_{(aq)}^- \rightarrow H_2O_{(l)}+\frac{1}{2}O_{2(g)}+2e^- \quad (5)$$

When the medium used is acidic however, the following half-cell reactions takes place:

$$\text{Cathodic Reaction: } 2H^+_{(aq)}+2e^- \rightarrow H_{2(g)} \quad (6)$$

$$\text{Anodic Reaction: } H_2O_{(l)} \rightarrow \frac{1}{2}O_{2(g)}+2H^+_{(aq)}+2e^- \quad (7)$$

The overall reaction can be summarized as:

$$H_2O_{(l)} \rightarrow \frac{1}{2}O_{2(g)}+H_{2(g)} \quad (8)$$

Figure 2. *Three most studied water splitting technologies [6].*

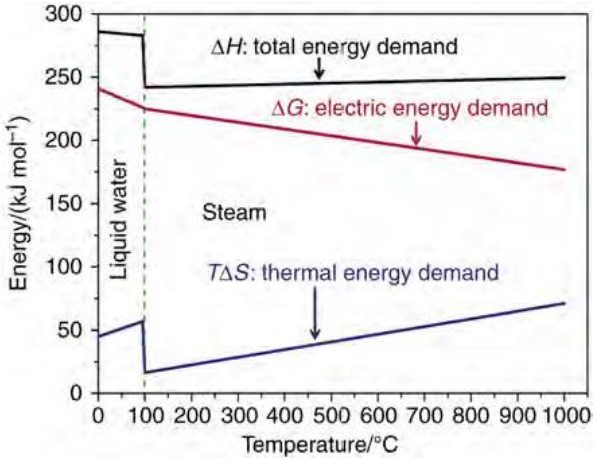

Figure 3. *Energy demand of a typical electrolytic water splitting [9].*

2.1. Electrolytic Water Splitting Technologies

Water electrolysis is a technique that utilizes electric current supplied externally to drive chemical water splitting reactions into hydrogen and oxygen. Ions in this technique at the surfaces of the electrodes either gain electrons (reduction) or losses electrons (oxidation), this results in the evolution of hydrogen at the cathode and oxygen at the anode. Hydrogen produced during this process can have purity as high as 99.9999% which contrasts with what is obtainable through other non-renewable hydrogen production methods where further treatments of hydrogen produced is required.

In 1789, using an electrostatic generator to produce an electrostatic discharge between two gold electrodes immersed in water, Jan Rudolph Deiman and Adriaan Paets van Troostwijk first demonstrated the first water electrolysis, however later development by Johann Wilhelm Ritte allowed for gaseous products separation [7].

Earlier technologies employed Alkaline as electrolytes and such persists till date, however proton exchange membrane technology which was first introduced by the General Electric in the Gemini project and other technologies like solid oxide and anion exchange membrane technologies have also emerged. In this section, the general thermodynamics principles, operating principles, challenges and recent advances with outlook of these technologies will be highlighted.

Water electrolysis is thermodynamically not possible as result it requires an input of external energy in the form of potential difference between the electrodes of the cell. By utilizing the Gibbs free energy equation to find the Gibbs free energy, the reversable voltage V_{rev} which is the minimum voltage required for electrolysis to take place can be calculated using the Gibbs free energy and the Thermoneutral Voltage V_{tn} which is the minimum potential difference required for electrolysis at constant temperature without necessarily an exchange of heat with the surrounding can be determined using the standard enthalpy [8].

$$\Delta G^{\circ}=\Delta H^{\circ}-T\Delta S^{\circ} \tag{9}$$

At standard conditions of temperature of 298.15 K and a pressure of 101.325 kPa, the standard enthalpy of formation (286.03 kJ mol^{-1}) and ideal gas entropy (0.163 kJ mol^{-1} K^{-1}) of gaseous water, the Standard Gibbs free energy is given as:

$$\Delta G^{\circ}=286.03-298.15\times 0.163$$

$$\Delta G^{\circ}=273.46 kJmol^{-1}$$

The reversable Voltage and thermoneutral voltages can be computed using the equations below, where F is faraday's constant (96485C) and n is the number of electrons transferred with a value of 2.

$$V_{rev}=-\frac{\Delta G^{\circ}}{nF} \tag{10}$$

$$V_{rev}=\frac{273.46}{(2\times 96485}$$

$$V_{rev}=-1.23V$$

This value requires that all components including the water feed be in gaseous form, however typical electrolysers operate at ambient conditions way below 80 degrees. Therefore, there is need for additional energy, and this additional energy is referred to as the thermoneutral voltage V_{tn} earlier defined and can be calculated as indicated below:

$$V_{tn}=-\frac{\Delta H^{\circ}}{nF}$$

$$V_{tn}=\frac{286.03}{2\times 96485}$$

$$V_{tn}=-1.48V$$

While 1.48V is enough to effect water electrolysis, the wa-

ter splitting reaction proceeds very slow and additional potential is required to speed up this process which is termed *overpotential* and inherently occurs due to low conductivity of the water and high activation energy of the water splitting process. For an efficient water splitting process over potential must be minimized as been implemented in alkaline electrolyzers by addition of salts to increase conductivity and the use of electrocatalysts to lower the activation energy in proton exchange membrane electrolyzers.

The efficiency of electrolytic water splitting technologies is calculated in two ways: the first being the faradaic efficiency which is the ratio of hydrogen produced to the amount of charge passed. A faradaic efficiency reading 100% simply translates that every electron produced during the oxidation was transferred to the reduction of proton to hydrogen gas which always fall short due to factors like hydrogen diffusion to the anode side and some parasitic electrochemical processes that are obtainable [10].

The energy efficiency is another method of calibrating the efficiency of a water splitting electrolytic system which seeks to measure the efficiency of the stack system by calculating the energy available by the produced hydrogen by using Hydrogen heating value (HHV) and dividing it by the amount of energy consumed by the cell during the production of the hydrogen. The equation for energy efficiency calculation is given by:

$$\eta_{eff}=\frac{\text{mole of hydrogen}\times HHV_{H_2}}{I\times V\times t}\times 100 \quad (11)$$

2.1.1. Basic Electrolytic Components for Hydrogen Production

Electrolyzers are electrochemical devices that utilizes external electrical energy to drive chemical reactions, here water electrolyzers are the main point of action which involves splitting water to produce hydrogen and oxygen. Typically, water splitting electrolyzers are fragmented into three levels which include the cell, stack and system levels.

The cell is the basic unit of the Electrolyzer which is composed mainly of a membrane sandwich between electrodes of cathode which is the hydrogen evolution electrode and the anode which is the oxygen evolution electrode. It also has porous layers for diffusion of products and bipolar plates for mechanical support and even distribution of flow.

Stack is a higher level of cell which is composition of two or more cells, usually connected in series with spacers, seals, frames and end plates that avoid leakages and spills.

System level goes beyond just the cell and stack of cells that makes an Electrolyzer, it includes equipment for converting input electricity like transformers or rectifiers, water treatment system, cooling systems, pumps and hydrogen purification systems.

In the following sections four most developed techniques of water electrolysis which include Proton exchange membrane, Alkaline water, Anion exchange and solid oxide electrolysis will be discussed citing there working principles, cost, challenges and prospects of the various technologies.

2.1.2. Alkaline Water Electrolysis (AWE)

Alkaline water electrolysis has been in existence since the 19th century with proven commercialization and maturity. This technology employs the use of 25-40 wt% of potassium hydroxide (KOH) and sodium hydroxide (NaOH) as electrolytes resulting in operating pH of the system to be between 13-14 [11].

Alkaline water electrolysis with a typical operating temperature of 60-80 ℃, this technology has a current density of about 0.1-0.5 A/cm^2 and can reach a lifetime of 90000 hours [12].

Major components include a separator/diaphragm typically made of asbestos diaphragm which was banned in the 1970s due health risk but nowadays we have inorganic ion exchange membranes Asbestos/Zirfon/Nickel coated stainless steel diaphragms [10]. other components are the stainless steel/nickel coated bipolar and end plates and a nickel mesh foam which is employed as the gas diffusion layer.

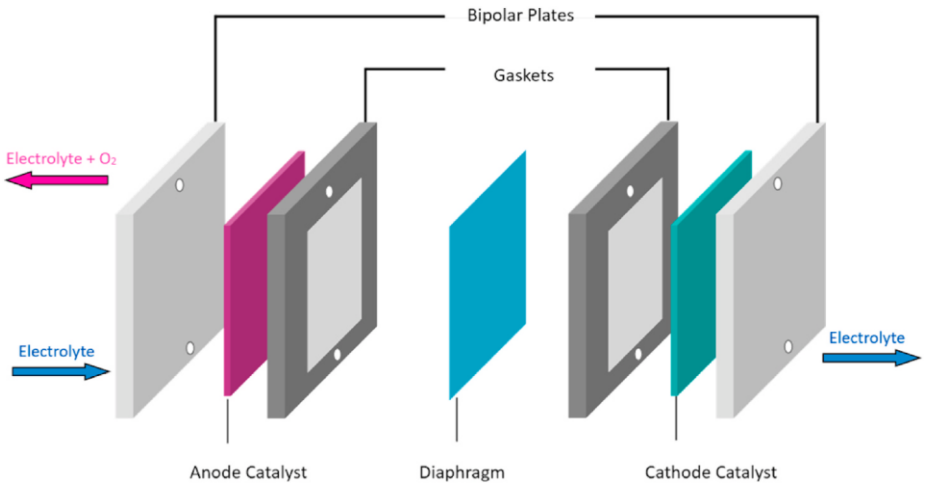

Figure 4. *Cell Components of Alkaline water electrolysis [13].*

Under an external electric current supplied, water is reduced at the cathode to release hydrogen and hydroxyl ions (OH^-). These released hydroxyl ions with the aid of the diaphragm separator travel to the anode where they are oxidized into oxygen gas and electrons released into the circuit as indicated in Figure 5.

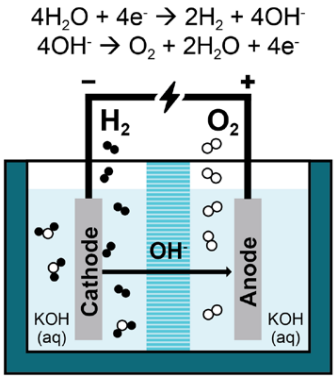

Figure 5. *Showing the simplified mechanism of Alkaline water electrolysis [14].*

Cost for alkaline water stack depends on the manufacturer but cost for the alkaline water electrolyzer typically is in the range 242 to 388 €/kW and may reduce to 52–79 €/kW by 2030 due to increase in current density, with the bipolar plates, Anode, cathode, diaphragm, stack assembly, balance and seals taking 30%, 5%, 8%, 7%, 13%, 12% and 25% of the total cost [15]. The alkaline water electrolyzers system could have a capital cost between 480 to 1450€/kW uninstalled cost but most often it's in the range of 480 to 720€/kW and such low cost could result in low levelized cost of hydrogen (LCOH) in the range of 4.80-5.0€/Kg H_2 [14].

Challenges and Future Outlooks: With a current density typically less than 0.6A/cm^2, these electrolyzers record an efficiency between 60-70% which is considered lower than other technologies [16]. Electrolyte management is a big challenge with this technology due to its corrosiveness and its sensitivity to Carbon dioxide gas that result in the precipitation of potassium Carbonate (K_2CO_3) at the gas diffusion layers thereby preventing further ion transferability [17].

Gas permeation or gas crossover have been identified as a challenge with alkaline water electrolysis, this refers to the process by which gas molecules move through the separator or diaphragm that divides the anode and cathode compartment [18]. Gas crossover in this technology is an undesirable phenomenon because such process exposes the system to possibles corrosion, explosion and the purity of the gas and hydrogen produced is compromised.

Current density is a measure of the amount of current passing through the cross sectional area of the electrode, this parameter is very important in the amount of hydrogen produced and consequently the overall performance of the cell. Its value is dependent on the temperature, voltage, pressure, concentration of electrolyte and the performance of the electrocatalyst. Optimizing one of this factors have found to improve the current density, [19] reported a current density of 3.75A/cm^2 at a voltage of 1.75V and a high temperature of 200 ℃. High temperature Alkaline water electrolysis have been related to increased reaction kinetics and sadly an extreme corrosivity which can be stabilized with the use of high corrosion resistance materials like stainless steel and a variety of Nickel Alloys [20].

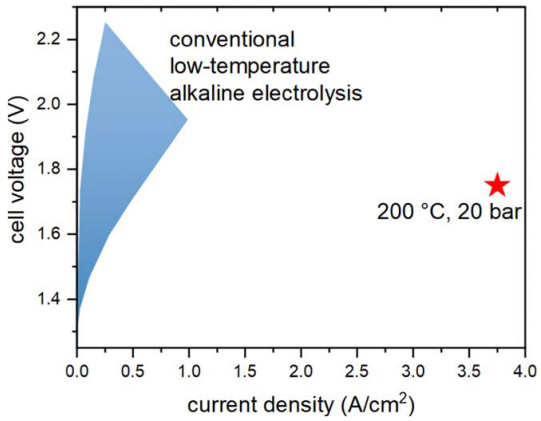

Figure 6. *Improvement of current density with rise in temperature compared to the conventional Alkaline electrolysis [18].*

Cost effective ruthenium (Ru) nanoparticles on copper plates acting as cathode have proven to enhances hydrogen adsorption and desorption. with stainless steel mesh acting as anode, these anodes were reported to record a current density of 3.7A/cm^2 at 2.0V [21]. Ni_3S_2 based electrocatalysts and Nafion binder and pt mass loading on platinum/carbon cathode and stainless steel anodes have significantly been highlighted with an improvement in the current density.

Corrosiveness of alkaline is a fundamental challenge that affects the overall performance and lifetime of the technology, over the years various studies have been conducted to resist such corrosiveness like the use of corrosion resistance materials like titanium, nickel, polymer, tantalum etc for the cell design [18].

Gas permeation of the cell have received advances in the use of separators with pore size less than 70nm and enough wettability and the construction of membranes with selective gas permeability and conducts ions greatly [13]. Strategies have been employed recently to overcome the cell's sensitivity to impurities which include; use of ions resin that removes contaminating cations and anions from water supply and the purification of water supply to remove metals affecting the electrode catalytic reactions [22, 23]; rebalancing the concentration of the electrolyte through the use of a supporting electrolyte [22]; employing dynamic cell operations and the use of

separated electrolyte cycles through automatic switching between operations [24].

2.1.3. Proton Exchange Membrane Electrolyzer (PEM)

In 1960s General electrics invented the proton exchange membrane also known as polymer electrolyte membrane. This technology employs the use of solid sulphonated polymer as electrolyte which acts as both the gas separator and electrolyte. Unlike in alkaline water electrolysis, PEM utilizes an acidic solid electrolyte and only deionized water is fed into the system [25].

PEM typically operates at temperatures between (30-80 ℃) at current density of 1-3A/cm^2 and producing hydrogen with purity reaching 99.9999% with the efficiency sometimes reaching up to 80% and a lifetime stability of up to 60000 hours [26]. Due to the electrodes pt layers, PEM has a faster hydrogen evolution reaction and offer more greater safety than the Alkaline water electrolysis.

Proton exchange membrane cell's components are typically composed of a membrane electrode assembly (MEA) which is made up of the membrane, cathode and anode electrodes. Other components are gas diffusion layer (GDL), bipolar plates and end plates. The popular membranes employed in PEM are of Nafion, Fumapem, Flemion, and Aciplex respectively. However, Nafion is the most widely used due its high current density, proton conductivity and high stability to mechanical and chemical stress [27]. The electrodes are made of precious metals especially the platinum group metals (PGM), the anode which is where the oxygen evolution reaction takes place is made up of electrocatalyst like Iradium (II) oxide (IrO_2) and the cathode, the location for hydrogen evolution reaction typically is composed of a carbon supported platinum (Pt).

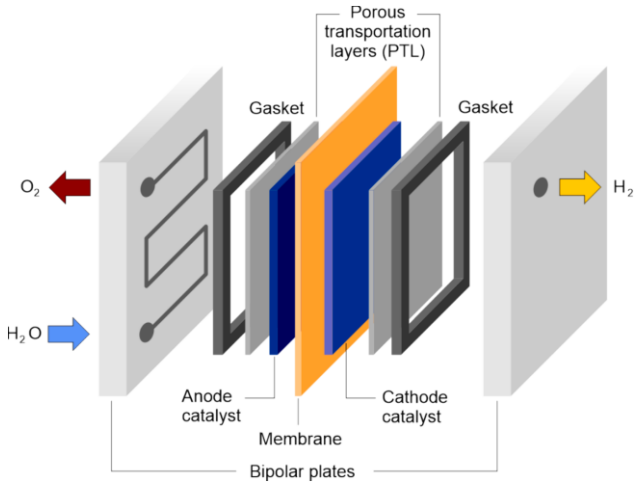

Figure 7. *Cell Components of PEM water electrolysis [28].*

Water is supplied to the cell through the anode where water is oxidized into protons and oxygen with the loss of electrons. These produced protons travel through the solid polymer to the cathode where they are reduced to hydrogen molecules as indicated in the Figure 8 below:

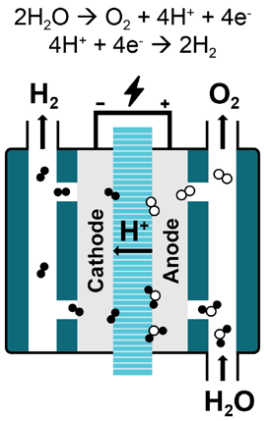

Figure 8. *showing the simplified mechanism of Proton exchange membrane electrolysis [14].*

The cost of PEM stack currently cost in the range of 384–1071 €/kW but may also reduce to 63–234 €/kW by 2030 [15]. However, the PEM Electrolyzer system have been reported to have an uninstalled capital cost of about 675-1060 €/kW which could result in the range of 5.80-6.90 €/kg H_2 [14].

Challenges and Future Outlooks: this technology can adequately contribute to load levelling by adjusting its operating current in response to fluctuation by offering high current during off-peak periods and low current during peak periods which makes it a perfect for a system that uses renewable electric supply [28]. However the advantages, the basic challenge associated with proton exchange membrane electrolysis lies on the cost and scarcity of materials use in the fabrication process of its components, for instance [29] highlighted that the usage of PGM as catalyst contributes to 40% of the total stack cost of a PEM.

Most recent innovations in the area of PEM focuses on reducing cost of the technology while improving durability and stability of the technology. Bipolar plates plays vital role in the technology, they most in addition to high conductivity be corrosion resistance, light weight, be gas impermeable and overall be low-cost [28]. Typical bipolar plates are made of titanium but recent studies suggested its oxidation into titanium oxide and stainless steel was posed as a possible replacement however, the coating of gold and platinum further increases the cost. Recently the coating of stainless steel with metal Nitrides like NbN, CrN/TiN, and TiN have shown for the development of the low-cost and high-anti-corrosion bipolar plates for Proton exchange membrane water electrolysis. [28, 30].

At a temperature of 80 degrees, acidic environment, a voltage of 2V and a high oxygen concentration, the current collector otherwise known as gas diffusion layer (GDL) most

have excellent chemical and physical properties. This GDL most exhibit great electrical conductivity with adequate corrosion resistance, however common materials employed at the anode are carbon materials which often most times undergo degradation due to corrosion and in turn affects interfacial contacts in the cell and the performance generally [31]. Recently, Titanium mesh have been identified as better current collectors and more promising are titanium modified current collectors with TiN/TiO_x, although care must be taken on the pore sizes of the gas diffusion layers as too small and too large could result in obstruction in gas removal and diffusion resistance and the hinderance of electron flow and water flow reaching the catalyst layer respectively [28].

Up to date perfluorosulfonic Acid membrane commercially referred to as Nafion is still the choice membrane, its organic chain end made composed of sulfonic acid enables its proton exchange facilitation when hydrated. Ability to exchange conduct protons by ion exchange capacity (IEC) is one of the most important properties of a good membrane and Nafion have been recorded to have about 0.9 mmol/g IEC, however, recent studies have focused on developing cost effective and durable membrane which are alternatives to the use of Nafion. Metal organic frame works, silica materials and TiO_2 on polymer and polymer mixed Nafion have identified as possible advancements of the Nafion membrane [32-34].

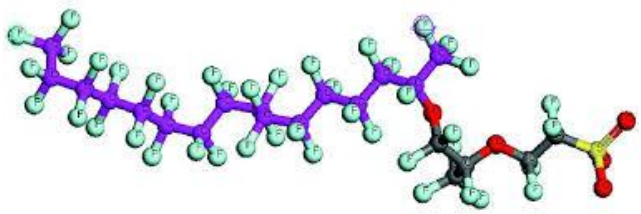

Figure 9. *chemical structure of Nafion [32].*

Hydrogen evolution reaction which occurs seamlessly is fast due to minimal amount of energy required for the reaction to occur, however, the oxygen evolution reaction is complex with requiring 4 electrons. This obstacle at the anode result in slow kinetics where overpotential is required to overcome the activation energy. Most times platinum is employed at the hydrogen evolution reaction while oxides, materials and alloys of scarce and high cost iridium (Ir) and ruthenium (Ru) have been used [35].

Studies have identified nano structures of Ir and Ru and blending of metals like nickel into the oxides of this precious metals have shown promising results, other structural forms of this metal like perovskite, pyrochlores and single atom dispersion have continue to draw attention in developing cost effective electrocatalysts.non-precious catalysts such as transition-metal sulfides, phosphides, carbides, nitrides, mixed metal oxides, and heteroatom-doped carbon materials are being explored as future alternatives to noble metals. However, their application is currently limited by poor stability and corrosion under strongly acidic and high-potential operating conditions, particularly at the anode. Consequently, these materials remain at the research and developmental stage, with no fully PGM-free PEM electrolyzer yet demonstrated for long-term operation.

2.1.4. Anion Exchange Membrane Electrolysis

This novel technology combines the principles of both proton exchange membrane electrolysis and alkaline water electrolysis. This technology employs a membrane between the cathode and anode only that it employs the use of transitional metals materials instead of platinum group metals which significantly reduces its capital cost. Unlike the alkaline which employs asbestos diaphragm, Anion exchange membrane uses a anion exchange membrane and they can operate under mild concentration of caustic soda or alkaline condition thereby minimizing the risk of leakages [36]. Although still at developmental stages, anion exchange membrane operates at low temperature and with very low stability time frame but its zero gap configuration results into higher current density due to a reduced ohmic resistance.

The cell like other technologies is typically made up of a current collector (gas diffusion layer), a membrane acting both as a separator and a medium for OH^- transportation, bipolar plates and end plates. The membrane is often quaternary ammonium ion exchange membranes like Sustanion, Fumasep and Fumatech as they are commercially known, while nickel or NiFeCo alloy materials are employed as electrocatalyst, nickel mesh/porous and carbon materials serves as gas diffusion layers with bipolar plates and end plates made from stainless steel and stainless steel coated nickel [27].

Water is introduced through the cathode where water is reduced to liberate hydrogen and hydroxyl OH^-, the hydroxyl travel through the membrane to the anode side where it is oxidized into oxygen and water as indicated in Figure 10.

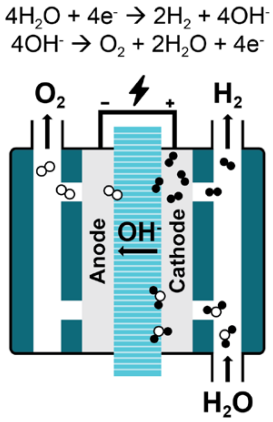

Figure 10. *showing the simplified mechanism of Anion exchange membrane electrolysis [14].*

Although the technological readiness level (TRL) of this technology is relatively low, studies have projected the cost to be about 200 €/kW [37]. The baseline levelized cost of hydrogen (LCOH) through AEM electrolysis is estimated at 5.20€/kg of Hydrogen, factoring in various operational trade-offs [38].

Challenges and Future Outlooks: Anion exchange membrane electrolysis is entirely a new technology with a recorded current density of 0.2-1 A/cm^2 and an ion conductivity of 0.1 S/cm. however, at a working temperature of 60-80 ℃, AEM electrolysis has a stability lifetime less than a thousand of hours. Key challenges associated with AEM includes the Alkaline stability, Specific-area resistance and ion conductivity issues [39].

For the overall development of anion exchange membrane electrolysis technology, researches most be employed towards increasing its ion conductivity to at least 10 S/cm, optimizing the cells for higher alkaline and thermal stability and overall its swelling and mechanical properties and most importantly it most be at lower cost and from a sustainable process.

It is important to note that increasing the AEM ion conductivity through high loading of functional group might leads to lower mechanical stability through swelling with water. [40] reported an ionic conduction of AEM of about 3 S/cm which its self-greater than what is obtainable in PEM water electrolysis. Most AEM are composed of N-containing positively charged groups like piperidinium, imidazolium and Ammonium or cations of not N-base like phosphonium, sulphonium and metal complexes [41]. Commercially available AEM include A201. Aemion, SUSTAINION, Orion TM1 and Fumasep. However, laboratory based PiperION and XION have been positioned to perform better than the current AEMs but cost will be a limiting factor due to low production scale. Several researches have been done in producing AEM with improve alkaline degradation stability, minimal thickness, PGM free electrocatalyst and an overall performance at a cheaper capital cost [11, 42, 43].

2.1.5. Solid Oxide Water Electrolysis

Introduced in 1970s in the United states of America by General electrics and Brookhaven National Laboratory, Solid oxide water electrolysis split water in the form of steam at a temperature between 500–850 ◦C drastically reducing the quantity of electricity needed to in a conventional electrolysis and hence higher efficiency [44]. Solid oxide electrolysis at that elevated temperature offers the advantage of a favourable thermodynamics and kinetics in comparison to other conventional techniques. This technology also gives the opportunity of integration with chemical synthesis plant where important green chemicals like methanol, dimethyl ether, Ammonia and others can be produced.

SOWE is primarily composed of three parts which include the porous electrodes and the solid ceramic material which act as the membrane for transport of oxygen ions during operation. The membrane is typically made of yttrium stabilized zirconia (YSZ) which conducts oxygen ions at elevated temperatures, often a solid solution with mol percentage of yttria Y_2O_3 on zirconia ZrO_2 while the hydrogen electrodes are typically Nickel and Yttrium stabilized zirconia composite metal like (Ni-YSZ). However, most oxygen evolution reaction anode are made of perovskite materials such as strontium-doped lanthanum manganite (LSM) and nickelates, are widely employed as cathode materials owing to their good oxygen reduction kinetics [27].

SOWE typically employs water in the form of steam to produce hydrogen at the cathode and oxygen at the anode respectively, steam is introduced at the cathode where it is reduced into hydrogen gas and oxide ion. hydrogen is released from the cathode and the oxide ion through the solid ceramic electrolyte diffuses to the anode where it is oxidized into oxygen and releasing electrons into the external circuit as indicated in Figure 11 below.

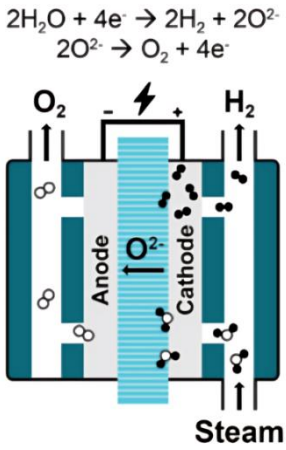

Figure 11. *showing the simplified mechanism of Solid oxide water electrolysis [14].*

The current hydrogen production cost of SOEC is €7–8 kg^{-1}, which is greater than that PEMWE and AWE. SOWE electrolyzers typically cost in the range of €2000-2500 depending on the manufacturer [14].

Challenges and Future Outlooks: with a reported stability of 20,000 hours and other favourable conditions SOWE offers a great opportunity for efficient hydrogen production. However, Solid oxide water electrolysis faces challenges like not energy efficient due to operation at very high temperatures, high cost, unstable electrodes and generally safety concerns.

Focuses have been in developing new electrode and electrolyte materials that do not only increases the optimal performance of SOWE at elevated temperatures but are also cost effectives. Materials like Scandia stabilized Zirconia (ScSZ), proton conducting oxides and Gadolinium Doped ceria (GDS) have been investigated as effective electrolytes due to their established carbon deposition tolerance, durability, and chemical compatibility [45]. Researches are ongoing on novel materials as electrode like Mn-doped Ruddlesden–Popper oxide

$La_{1.5}Sr_{0.5}NiO_{4+\delta}$ (LSNMx), perovskite-based rare earth nickelates of $Ln_2NiO_{4+\delta}$ (Ln = La, Pr, and Nd) and Ni-$Zr_{0.92}Y_{0.08}O_{2-\delta}$ | $Zr_{0.92}$ $Y_{0.08}O_{2-\delta}$ | $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ | $Pr_{0.6}Sr_{0.4}CoO_{3-\delta}$ have been studied and posed as excellent alternative electrodes for solid oxide electrolysis [46]. Strategies like nano structuring and incorporation of catalyst or surface modification further aims to improve the reaction kinetics and overall the hydrogen production efficiency of solid oxide electrolysis for hydrogen production.

2.1.6. Cost Reduction Strategies of different Electrolytic Technologies

Table 1. Cost Reduction Strategies of different electrolytic technologies for water splitting [14].

	AWE	PEM	AEM	SOWE
Capital cost	Utilizations of cell components that increases the current density of the cell while still maintaining a reliable efficiency.	Reducing catalyst loading. Utilizing thinner membranes and integration with renewable energies. Widespread manufacturing at large scale	Platinum Group metals free electrodes with high activity and selectivity.	Developing cost effective materials and fabrication process. Develop lower temperature operational conditions. System design of low cost.
Performance	Developing systems that manages gas permeability problem of the cells. Engineered novel separators and catalyst material. Explore the design of novel cell or stack design.	High performance membrane with efficient interfaces. Increased catalyst activity and selectivity. Optimized porous layers for optimal transport of materials and products	Eliminating electrolytes and components integration.	Decrease cell resistance. Enhancing material contact. Developing thermal integrations
Stability	Consideration of different operating conditions of the cell. Exploring new designs. Research in development of generally new materials.	Putting into place stress testing process which is reliable. Optimization of the membrane, catalyst layer and gas diffusion layer. Developing durability test under different testing conditions that are in line with the reality of operations.	Development highly durable cell or stack components	Operating temperature reductions. Reducing electrode contamination. Improving material stability.

2.1.7. Comparative Characterization of Electrolytic Hydrogen Production Methods

In this section of the review electrolytic technologies will be characterized in comparison to each other as summarized in the table below.

Table 2. Comparative characterization of electrolytic hydrogen production technologies.

	AWE	PEM	AEM	SOWE
Electrolyte	KOH/NaOH	Solid Polymer	H_2O/ 1M KOH	Ceramic solid
Separator	Asbestos/Zirfon	Nafion	Ionomer	YSZ
Temperature	70-100 ℃	50-80 ℃	40-80 ℃	500-1000 ℃
Current density	0.2-0.8A/cm^2	0.5-10 A/cm^2	0.2-2.0 A/cm^2	0.2-1.3 A/cm^2
Voltage	1.8-2.4V	1.4-2.3V	1.4-2.0V	0.7-1.5V
Efficiency	62-84%	55-80%	70-80%	>90%
Pressure (bar)	2-10	30-80	30-80	<30

	AWE	PEM	AEM	SOWE
Hydrogen purity	99.5–99.9998%	99.9–99.9999%	99.9–99.9999%	99.9%
Charge carrier	OH^-	H^+	OH^-	O^-
Anode reaction	$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$	$2H_2O \rightarrow O_2 + 4e^- + 4H^+$	$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$	$2O^{2-} \rightarrow O_2 + 4e^-$
Anode electrode	Ni, Fe, Ni alloys	IrO_2	Ni–Fe alloys	Perovskites, LSM
Cathode reaction	$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$	$4H^+ + 4e^- \rightarrow 2H_2$	$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$	$2H_2O + 4e^- \rightarrow 2H_2 + 2O^{2-}$
Cathode electrode	Ni, Ni alloys	Platinum Pt/C	Pt–Ni, Ni–Mo	Ni, YSZ,
Stack Stability (h)	60,000–100,000	50,000–100,000	>30,000	>40,000
TRL	TRL 9	TRL 9	TRL 6	TRL 7-8
Pros	Low capital cost. Matured technology. Nonprecious metals usage. Relatively high stability.	High current density. Higher pressure tolerance. Quick startup time. High hydrogen purity. Compact design.	Low material cost. Low gas permeability. Low ohmic resistance. High current density. High performance. Low corrosivity	Fast reaction kinetics. Duel reversibility (Electrolyzer/fuel cell). High efficiency. Lower catalyst cost.
Cons	Impurities sensitivity in water. Gas permeation. Low current density. Slow start up time.	Low durability due to acidic environment. High capital cost from use of precious metal catalysts	Low stability and durability. Alkaline degradation. Low technology readiness level.	High capital investment. Durability issues. Developing technology and high temperature requirement

2.2. Photocatalytic Water Splitting

Photo-assisted water splitting was first demonstrated in 1972, Honda and Fujishima demonstrated with the use of TiO_2, how water can be split into hydrogen and oxygen when it was irradiated with ultraviolet (UV) light. However, UV light makes up just a small fraction of the solar radiation that reaches the earth surface, there was need for fabrication of materials and photocatalyst that have the ability of absorbing wider range of wavelength of light in the electromagnetic spectrum. Photocatalysis is sometimes considered as an artificial photosynthesis as the process seeks to emulate natural photosynthesis. This process is thermodynamically unfavourable as indicated by the equation below, however, semiconductors are utilized as catalysts exploring the nature of their electronic configuration [6].

$$H_2O + h\nu \rightarrow H_2 + \frac{1}{2}O_2,\ \Delta G^\circ = +273\ kJmol^{-1} \quad (12)$$

A photocatalyst system typically consist of a photocatalysts like TiO_2 well known for good UV light absorption, graphitic carbon Nitride (C_3N_4) [47], Cadmium Sulphide (CdS) [48], perovskite material like ($SrTiO_3$, $BaTaO_2N$) [49] or recently Bismuth-based materials ($BiVO_4$, Bi_2WO_6) [50]. A photocatalyst consist of an electronic system with a lower energy level known as valence band and a higher energy level known as the conduction band. The distance between the valence band and conduction band called the band gap is an important parameter that influence the efficiency of photocatalyst which is normally a semiconductor should be 1.23ev but for energy losses sake broader band gaps of 1.5-2.5ev are often considered.

In principle, photocatalytic hydrogen production occur when photocatalyst is irradiated with sunlight, this irradiation if equal or greater than the band gap energy result into promotion of electrons in the valence band into conduction thereby creating charge separation due to promoted electrons. There exist holes in the valence band and electrons conduction that if transported to the surface of the semiconductor result in the reduction and oxidation of water respectively.

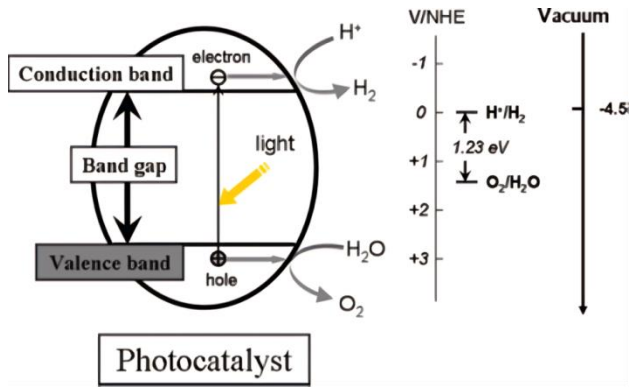

Figure 12. *Fundamental principle of photocatalytic hydrogen production [51].*

To ensure oxidation and reduction of water by the electrons and holes respectively, the match of the band gap and the potentials of both the valence band and the conduction must be appropriate [51]. For instance, the reduction potential of the bottom level of the conduction band must be more negative than the normal hydrogen electrode (NHE) while the top of the valence band most have a reduction potential more positive than the oxidation potential of water.

After photoexcitation, excited electrons and holes separate and migrate to the surface where they act as the reducing and oxidizing agents respectively. However, recombination reactions of charges limit hydrogen generation and compete with the process but addition of sulfuric acid and glycerol have been reported to reduce recombination rates with other hole scavengers like sodium sulphate, methanol, and ethylenediamine also proving effective.

Efficiency of photocatalytic hydrogen production can be measured directly by measuring the overall amount of hydrogen produced as indicated in the equation below.

$$\frac{\text{output energy of hydrogen evolved}}{\text{input energy of incident light}} \times 100 \quad (13)$$

This efficiency is greatly affected by several factors as highlighted by [6], which include the amount of photocatalyst, the efficiency of the separation of charges, their transportation and the surface area of the photocatalyst for adsorption.

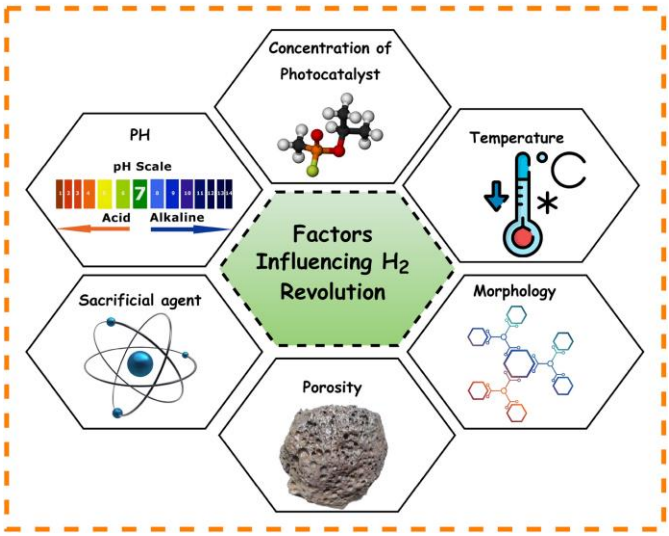

Figure 13. *Summary of factors that affect efficiency of photocatalytic hydrogen production [6].*

Recent Advances and Future outlooks: as a promising sustainable and clean way of producing energy there is need for development of materials that are scalable and cost-effective through fabrication of photocatalyst that are not only having high activity but also photocatalysts who are stable to defects like photo corrosion. Recent studies has seen the use of Graphitic carbon nitride (g-C_3N_4) due to their high stability and wide range of light absorption in the visible region of the electromagnetic spectrum [52]. Doped metal oxides, perovskite materials and heterojunction semiconductor materials have shown excellent result in charge separation and thereby increasing the efficiency of photocatalytic hydrogen production [53-55].

The tuneable and large surface area properties of metal organic frame works has shown great results also in the photocatalytic hydrogen production. Although expensive, using precious metals like gold and silver have been considered options to improve light absorption and consequently charge transfer. There is also an integrated call for the usage of photocatalysis in the reduction of CO_2 for sustainable fuel production. Future researches should focus on improving the overall efficiency, scalability and sustainability of the technology through advance materials like For instance, a study highlighted the use of MOF-derived metal oxide heterojunctions as efficient photocatalysts for hydrogen production [56].

2.3. Artificial Photosynthesis (Photoelectrochemical)

Artificial photosynthesis is a biochemical process that uses the principle of natural photosynthesis that converts the sun's energy, CO_2 and H_2O to O_2 and carbohydrates. Photosynthesis which is broken to ''photo'' and ''synthesis'' used in plants and other organisms transforms light into biochemical energy which is later stored in the form of carbohydrates [57]. Photosynthesis is broken into four processes. These processes are light harvesting, charge separation, water splitting, and fuel productions [58].

In Artificial photosynthesis, photosensitizers such as semiconductors like TiO_2, molecular dyes, or quantum dots are used to capture the solar energy which is used to separate the charge carriers. The positive charge carriers spilt the water into Hydrogen ions and oxygen molecules.

If the man-made solar energy (artificial photosynthesis) is appropriately developed it will provide a much higher efficiency. For industrial feasibility for artificial photosynthesis, an efficiency of 10% is required but Bio Solar Cells, a Dutch research program has researched an estimated theoretical efficiency of up to 40%. [58].

The principle of artificial photosynthesis is carried out in a photoelectrochemical (PEC) cell which combines the function of a photovoltaic cell and an Electrolyzer.

When sunlight hits the panels, the nanoparticles generate electro-hole pairs which initiate the water splitting process resulting into the production of hydrogen and oxygen. In detail, Light-harvesting complexes such as porphyrins (arrays of chromophores) absorb photons and transfer the excitation energy to a reaction centre where chemical reactions occur. After the photons are absorbed, excitation takes place using energy. This process is important to drive the conversion of water and carbon dioxide into fuels using the energy generated.

Water is then split into oxygen and provides electrons in the reduction of carbon oxide or other substrates to form fuels like hydrogen or hydrocarbons. Catalysts are introduced to facilitate the chemical reactions in the conversion of captured energy into chemical fuels. These catalysts can be based on precious metals or biomimetic enzymes that enhance the efficiency of the reactions.

Effective artificial photosynthesis often involves linking two separate cycles: one that generates a fuel (e.g., hydrogen) and another that provides the oxidizing agent (e.g., oxygen). This integration is essential for creating a functional and efficient system. To ensure longevity and efficiency, artificial photosynthesis systems may incorporate built-in protection and repair mechanisms to address photochemical damage. This could involve redundancy in the system design or the development of artificial repair enzymes.

This step is carried out in a photoelectrochemical (PEC) cell which combines the function of a photovoltaic cell and an Electrolyzer. At the photoanode, water molecules are oxidized to produce oxygen, protons and electrons whereas at the photocathode, the protons and electrons combine to form hydrogen gas. The diagram below shows the working principle of an artificial photosynthesis.

The reaction equations are provided below:

$$6CO_{2(g)}+6H_2O_{(l)} \xrightarrow{\text{light+artificial pigment}} O_{2(g)}+C_6H_{12}O_6 \quad (14)$$

$$C_6H_{12}O_6+6H_2O_{(l)} \xrightarrow{\text{light+artificial pigment}} 6CO_{2(g)}+6H_{2(g)} \quad (15)$$

Challenges and Future Outlook

Artificial photosynthesis has the advantages of being renewable, sustainable, with water source flexibility and cost effectiveness. However, Current artificial photosynthesis systems struggle to achieve the efficiency levels of natural photosynthesis. While natural photosynthesis operates at about 0.1% efficiency, replicating this in artificial systems remains a significant challenge. There is a need for suitable catalysts that can effectively facilitate the conversion of solar energy into chemical energy. Research is ongoing to develop catalysts that can efficiently mediate water splitting and CO_2 reduction, but many existing catalysts still face performance limitations. [57].

Efficiently capturing a broad spectrum of sunlight and transferring electrons to the reaction centers are critical challenges. The design of photocathodes and other components must be optimized to enhance light absorption and electron mobility . The processes of splitting water and reducing carbon dioxide are complex and require significant energy input. Overcoming the thermodynamic and kinetic barriers associated with these reactions is essential for practical applications [59].

For artificial photosynthesis to be competitive future research should focuses on designing and developing highly efficient, stable, and low-cost photocatalysts (e.g., perovskites, metal oxides, and metal-organic frameworks), designing artificial photosynthtic systems that can overcome photocorrosion and degradation of catalysts, Scalable and cost-effective manufacturing processes and with easy Integration with existing renewable energy infrastructures.

Table 3. Comparative summary of of characteristics of water spliitng technologies.

Characteristics	Electrolysis	Photocatalysis	Photoelectrochemistry
Type of light	Indirect	Direct	Direct
Scalability	High	Moderate	Moderate
Cost	Moderate to high	Potentially low	High
Efficiency	Potentially high	Typically low	Moderate
Benefits	Durable and high stability. Scalable easily. Convenient downstream process. Improved efficiency.	Most ideal for H_2 production. Clean and sustainable energy is generated. Low complexity. Zero greenhouse gas emission.	Very simple downstream process. Improved efficiency. Increased durability. Very little environmental impact.
Key Challenges	Higher environmental impacts as compared other technologies. High cost. Complex system.	New research area. Catalyst photo corrosion. Not quite stable. Very low efficiency. Gas separation problem. Issues with scalability.	Long time stability is not guaranteed. Very high cost. Highly complex.

3. Biological Methods of Hydrogen Production

Biomass is referred to as a carbon neutral and sustainable feedstock derived from plants, animals and microorganism and their waste product and, waste produced from agriculture and forestry activities such as agricultural residues, forest remains, energy crops, agro-industrial waste, and municipal waste [60]. Biomass being the product of photosynthesis, the CO_2 from biomass returns to the atmosphere at the end of the process leading to almost a neutral emissions scenario.

3.1. Biophotolysis

This method relies on the recreation of phenomenon of photosynthesis, where water is split into hydrogen and oxygen in the presence of light. Only that in Biophotolysis such process is carried out by microorganisms such as algae and cyanobacteria. Green algae and cyanobacteria like Chlamydomonas reinhardtii, Scenedesmus obliquus, Chlorella vulgaris, Anabaena variabilis, Synechocystis sp. PCC 6803, Nostoc sp and Rhodopseudomonas palustris use the energy of sunlight to produce either carbohydrates (photosynthesis) or, under special conditions, hydrogen (biophotolysis) by splitting water [61].

Biophotolysis is divided into two broad operating principles which include either direct biophotolysis or indirect biophotolysis.

Direct Biophotolysis: in direct biophotolysis microorganisms under anaerobic conditions are able to split water with the aid of sunlight as indicated in the equation below:

$$2H_2O + \text{Light Energy} \xrightarrow{\text{Algea or Cyano bacteria}} H_2 + O_2 \quad (16)$$

This form of biophotolysis were oxygenic photosynthesis takes place is characterized by two reactions which take place in the photo-system I and II which all together are responsible for splitting water and evolving hydrogen and oxygen. When electron are generated from the photosystem I they are transported to the photosystem II were the hydrogenase enzyme produces hydrogen. Green algae are one of the microorganisms with hydrogenase and therefore are able to produce hydrogen from, however systems without hydrogenase enzymes only oxygen is produced. Direct biophotolysis is demonstrated in the figure below:

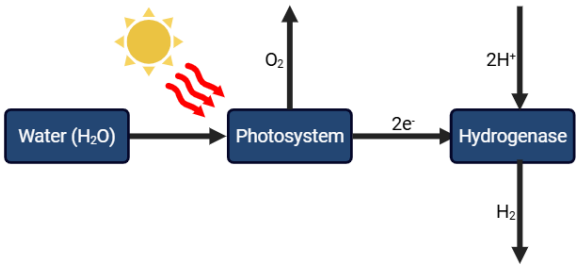

Figure 14. Direct Biophotolysis.

Indirect Biophotolysis: indirect biophotolysis is carried out by microorganisms under anoxic conditions were they can produce hydrogen under fermentation. This process involves two step name; I) oxygen evolution and the fixation of carbon

dioxide into cell materials such as carbohydrates and lipids; and II) the second step occurs in a dark fermentation or a combination of dark fermentation and photo fermentation bioreactor where the produced carbohydrates are converted into acetic acid where it is then completely transformed into hydrogen and carbon dioxide with the aid of light under anaerobic conditions in a photo(heterotrophic) bioreactor.

Equations of reaction is given as follows:

$$\text{First step: } 6H_2O+6CO_2 \xrightarrow{\text{Light}} C_6H_{12}O_6+6O_2 \quad (17)$$

$$\text{Second step: } C_6H_{12}O_6+6H_2O \xrightarrow{\text{Light}} 12H_2+6CO_2 \quad (18)$$

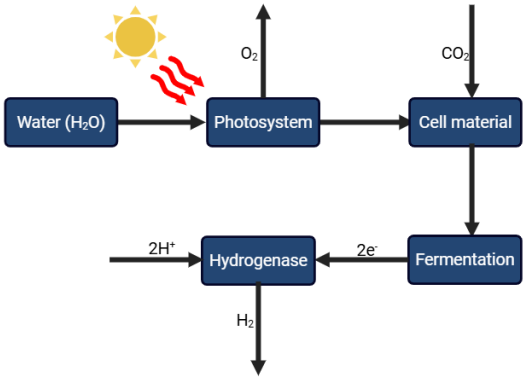

Figure 15. *indirect Biophotolysis.*

Challenges and Future outlook

Biophotolysis is generally an attractive and a green way of producing hydrogen, since it utilizes and converts abundant sunlight, subrates and water into hydrogen without a release of any greenhouse gas. However, biophotolysis is still at a developmental stage especially in research laboratories. For instance both types of biophotolysis have photochemical conversion of sunlight to hydrogen between 1.5 to 10 % with very low hydrogen production rate although with research efforts aiming to increase this value to 20% biophotolysis might in future compete with other sustainable technologies of producing hydrogen.

Research efforts in the development of genetically modified microorganisms that will efficiently produce hydrogen is the new direction, this genetically modified organisms should be able to withstand the inhibition of these microorganisms that is caused by oxygen. Optimization of bioreactors conditions is one area of research interest were efficient membrane separation and photoreactors are designed to increase the overall hydrogen yield. scalable and cost effectiveness of biophotolysis should be investigated for easy integration with other renewable energy sources for a more sustainable energy transition.

3.2. Fermentation

Generally fermentation is the decomposition of organic matter into alcohols, methane/other gases, organic acids etc under the influence of microorganisms usually in the absence of oxygen. Carbohydrates are commonly the substrates for fermentation. Fermentative hydrogen production is a biological process where microorganisms, primarily anaerobic bacteria, break down organic matter to produce hydrogen gas (H_2). This process occurs in the absence of oxygen and is a promising method for sustainable hydrogen production using organic waste, agricultural residues, or industrial byproducts [62].

Usually at a temperature of Mesophilic (30–40 ℃) or thermophilic (50–60 ℃) conditions, Organic materials like glucose, starch, food waste, wastewater sludge, or lignocellulosic biomass are acted on by Hydrogen-producing bacteria such as *Clostridium*, *Enterobacter*, and *Escherichia coli* to produce biohydrogen at pH Optimal range of 5.0–7.0.

Fermentative hydrogen proceeds in two pathways either through Photo Fermentation or through dark fermentation.

Dark Fermentation: this pathway of hydrogen production under anaerobic conditions involves biochemical biomass conversion. In the first biochemical anaerobic process complex organic materials that can not be utilize by bacteria are broken down into simpler units like amino acids and monosaccharides by anaerobes *Bacteroides*, *Clostridia*, and other facultative bacteria. In this first step of hydrolysis, the speed of hydrolysis cheaply depends on the nature of the substrate employed as carbohydrate-based substrates are generally easy to decompose than proteinous substrates [63].

The second phase of dark fermentation involves the acidogenic bacteria acting on the products of hydrolysis to produce short chain organic acids like acetic acid, propanoic acid, butyric acid, some alcohols, CO_2 and most importantly hydrogen. In all this stage converts amino acids, fatty acids and organic acids into acetate, Hydrogen (70%), alcohols(30%) as well as some volatile fatty acids [64].

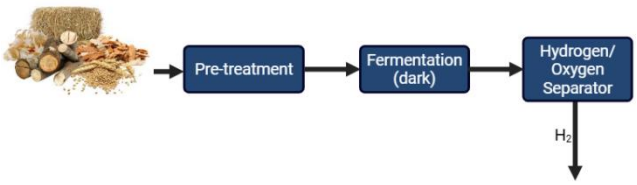

Figure 16. *Dark fermentation Scheme.*

This process can occur in a single reactor where hydrolysis, acidogenesis, and acetogenesis takes place, however keeping the microorganisms in check is the main challenge in this strategy because the microorganisms differ in terms of physiology, nutritional needs, growth kinetics, and sensitivity towards environmental conditions. The multistage strategy with different reactors is more effective and control inhabitants.

Photo Fermentation: in photo fermentation photosynthetic bacteria act through a sequence of biochemical reactions on organic substrates to produce hydrogen. Through the action of the nitrogenise of these bacteria, they have the potential of

converting organic substrates into hydrogen in three steps biochemical reactions similar to those listed in dark fermentation [65].

Photo fermentation process scheme is demonstrated in the figure below.

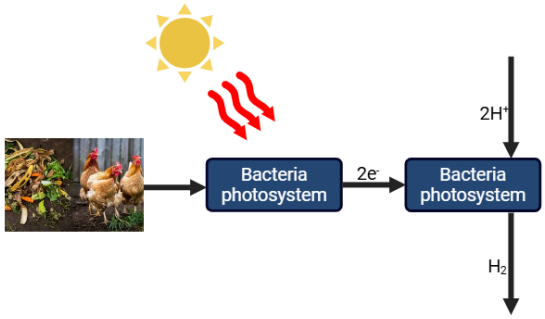

Figure 17. *Photo fermentation process scheme.*

Challenges and Future outlook

One of the advantages of fermentative hydrogen production is its broad range of substrates that can be employed, however, this technique is greatly influenced by factors such as temperature, pH, nutrients, inoculum and enrichment conditions, residence time, and hydrogen partial pressure which cumulatively reduce the overall hydrogen production yield typically 2–3 mol H_2 per mol glucose, compared to theoretical 12 mol [66].

Photo fermentation requires continuous light supply which is not possible at night with noticeable slow grow rate of photosynthetic bacteria. Nitrogenase are opened to oxygen inhibition which makes the system highly oxygen sensitive. With a very low hydrogen yield, dark fermentation experience competing microbial pathways and accumulations of volatile fatty acids further reduces the production of hydrogen and even if produced they at risk of consumption by methanogens.

Future researches aims to optimize the various conditions of temperature and pH for a better hydrogen yield . researchers in the field of culturing selective microbes that inhibit microbial path ways competition and also inhibit side hydrogen consumers. There is need for a combination of the two pathways into a hybrid technology for a more improve hydrogen yield production. Scientists are working on improving hydrogen yields, optimizing microbial strains, and integrating new technologies for large-scale applications.

3.3. Gasification

Gasification is the process of converting organic or fossil-based carbonaceous substances at high temperatures without combustion, with a controlled amount of oxygen and /or steam into CO, H_2 and CO_2. Carbon monoxide then reacts with water to form carbon dioxide and more hydrogen through a water-gas shift reaction. Absorber or special membranes can separate the hydrogen from this gas stream. The gas may also contain particulate matter, which is removed using cyclones and scrubbers. The particulate free gas is compressed and then catalytically steam reformed to eliminate the tars and higher hydrocarbons. This is followed by high and low temperature shift conversion reactions to produce additional hydrogen. Finally, hydrogen is separated from other products by pressure swing adsorption.

The main reaction equation is given by:

$$C_{(s)}(Biomass)+H_2O_{(g)} \leftrightarrows CO_{(g)}+H_{2(g)} \quad (19)$$

$$CO_{(s)}+H_2O_{(g)} \leftrightarrows CO_{2(g)}+H_{2(g)} \quad (20)$$

The biomass gasification reactor operates at 850 ℃ to produce a lot of syngas. The chemical composition of the biomass is important in the balancing of the reaction's biomass.

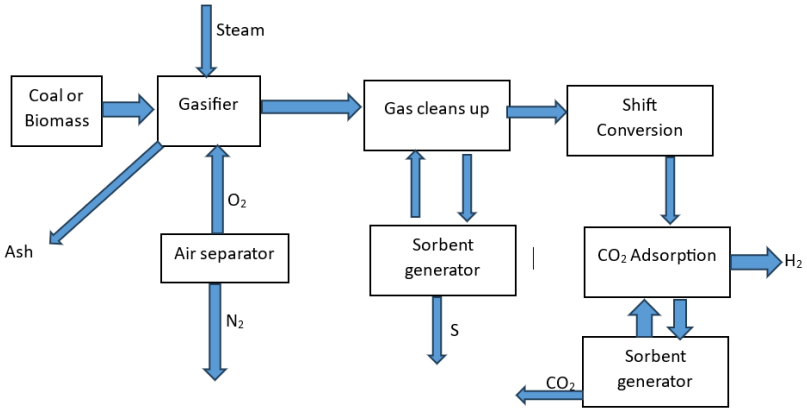

Figure 18. *Gasification Scheme of Hydrogen production.*

Challenges and Future Outlook

Gasification occur at very high temperatures, incomplete gasification results into formations of tars, chars and unreacted carbon. This challenge generally leads to low hydrogen

yield. Most biomass and wastes which are used as feedstocks are not always the same, the inconsistency in the feedstock greatly affects the gasification's efficiency [60].

Further purification requirements, waste mangement and use of high efficient catalyst further increase the capital cost of this technology especially at a large scale. Biomass gasification can produce high-purity hydrogen. European Environmental Agency (ENEA) is developing innovative solutions for gas cleaning and conditioning where Biomass gasification can utilize low-cost and low-valued feedstock. ENEA is involved in EU projects (UNIfHY, BLAZE, GICO) to demonstrate biomass gasification for hydrogen production. Production costs of 3-6 €/kgH2 are estimated for plants of 10 MW size [67].

Gasification remains a promising pathway for hydrogen production, especially from biomass and waste. Future research is centred on improving efficiency, reducing costs, and minimizing environmental impact through developing advanced gasification technologies like Plasma Gasification, Supercritical Water Gasification (SCWG) and Chemical Looping Gasification (CLG). Innovative ways of feedstock characterization and pre-treatment will be valuable in improving the overall hydrogen production yield.

3.4. Pyrolysis

Pyrolysis is a thermochemical process that breaks down biomass (wood chips or agricultural residue which are lignocellulosic biomass as raw materials) at high temperatures without oxygen, producing gases, bio-oil and biochar as the products.

The conventional approach is divided into four types. These are slow pyrolysis, fast pyrolysis, flash pyrolysis and intermediate pyrolysis. Fast pyrolysis is particularly effective for maximizing the yield of gaseous products, including hydrogen. Pyrolysis heating rate (HR), temperature and time, residence time of volatiles, and feedstock size are the parameters that differs from the different processes [68].

Slow pyrolysis: This process is carried out at a temperature between 300-700 ℃, with a residence time of >5min. This means it can hold for 5mins. It has a feedstock size varying from 5 to 50mm therefore feedstocks such as macroalgae, herbaceous and woody biomass can be used. Intermediate pyrolysis operates at a temperature up to 500 ℃ with a process time between 30-150s [69]. Fast pyrolysis operates at a temperature between 450-800 ℃ with a residence time of 0.5-1.0s [70].

Biomass is thermally decomposed in the absence of air at elevated temperatures (typically between 300 ℃ to 900 ℃). During pyrolysis, biomass is converted into three main types of products: solid (biochar), liquid (bio-oil), and gaseous products. The gaseous products contain a mixture of hydrogen, carbon monoxide, methane, and other hydrocarbons. The yield of hydrogen in the gaseous phase can be influenced by the temperature and the presence of catalysts. The use of catalysts is crucial for improving hydrogen production. Catalysts can help inhibit the formation of tar and promote the conversion of volatile compounds into hydrogen-rich gases. Common catalysts include metal oxides and other materials that facilitate the breakdown of complex organic molecules.

Higher temperatures and longer residence times during the pyrolysis process favour the production of hydrogen. The optimization of these parameters is essential to maximize hydrogen yield.

Challenges and Future Outlook

The variability in biomass composition can lead to inconsistent hydrogen production results, complicating the standardization of the pyrolysis process. This further, increases the production of tar during pyrolysis and poses a significant challenge, as it can inhibit catalyst activity and reduce the overall efficiency of hydrogen production [71].

The hydrogen yield from pyrolysis is relatively low (5-10 g of H_2 per 100 g of biomass) compared to other methods like gasification, which can make the process less economically viable. Also, the expense associated with catalysts, which are crucial for enhancing hydrogen production, can significantly impact the economic feasibility of the pyrolysis process. The production of hydrogen through pyrolysis faces economic challenges primarily due to high catalyst costs, which are essential for enhancing hydrogen yield. The costs associated with catalysts can significantly impact the overall economic feasibility of the pyrolysis process for hydrogen production. Additionally, there are separation and purification costs involved in extracting hydrogen from the gaseous products, which can also contribute to the overall expenses of hydrogen production [72].

These approaches which are catalytic pyrolysis, co-pyrolysis, hydro-pyrolysis and microwave pyrolysis and autothermal pyrolysis are in practice currently. These processes are modified conventional processes. According to research, advanced approaches, such as CFP, hydro pyrolysis, are suitable for producing high quality bio-oil and microwave, catalytic and co-pyrolysis can be considered as pathways to maximize H_2 yields.

Researching more affordable catalysts, process intensification, and automation. And Large-Scale Deployment & Policy Support will greatly increase the adoption of pyrolytic technology for hydrogen production.

Table 4. Comparative Summary of the characteristics of biological methods of hydrogen production.

Feature	Biophotolysis (Direct and Indirect)	Fermentation (Dark and Photo)	Gasification	Pyrolysis
Temperature ℃	20-30	30-30	700-1000	300-700
Hydrogen Yield (mol H_2/mol substrate)	Low (≤ 2)	Moderate (2–4)	High (10–20)	High (10–15)
pH	Neutral (~7)	5–8	-	-
Type of Substrate	Water, Organic Waste	Biomass, Organic Waste	Biomass	Biomass
Catalyst	Enzymes, Light	None or Enzymes	Metal Catalysts	None or Metal Catalysts
Complexity	High	Moderate	High	moderate
Technology Readiness Level (TRL)	Low (Lab Scale)	Moderate (Pilot Scale)	High (Commercial)	High (Commercial)
Cost	High	Moderate	High	Moderate
Hydrogen Purity	High	Moderate (Needs Purification)	High	Moderate
Challenges	Low efficiency, Oxygen Sensitivity	Low Yield, By-Products Formation	High Cost, Tar Formation, high reactor Cost, problems related to corrosion and plugging, and difficulty to recover the catalysts.	High Energy Demand, Tar Formation
Advantages	Requires simple cultivation, Simple substrate of H_2O, CO_2 consumption, Renewable and Sustainable	Uses Waste, Scalable, Process a variety of substrates, No O_2 limitation issues and Bioremediation	High Hydrogen Yield.	High Hydrogen Yield, Can Use Mixed Waste.

4. Critical Comparison of Water Splitting and Biological Technologies for Hydrogen Production

4.1. Efficiency and Yield

Water Splitting: Electrolytic water splitting, particularly solid oxide electrolysis (SOEC) and proton exchange membrane (PEM) electrolysis, offer high efficiencies (>80%) with high-purity hydrogen (>99.9%). Photocatalytic and photoelectrochemical (PEC) water splitting, while promising, remain limited by their low efficiency (<5%) due to charge recombination losses.

Biological Methods: Among biological technologies, gasification and pyrolysis achieve higher hydrogen yields (~10-20 mol H_2/mol substrate) than fermentation and biophotolysis, but they require higher temperatures (700–1000 ℃). Biophotolysis and fermentation, though sustainable, produce lower hydrogen yields (≤2–4 mol H_2/mol substrate) and suffer from substrate dependency.

4.2. Cost and Scalability

Water Splitting: Electrolysis (PEM, alkaline, SOEC) is commercially scalable, with alkaline electrolysis (AWE) being the most cost-effective at €242–388/kW. However, PEM electrolysis remains expensive due to platinum group metal (PGM) catalysts, and SOEC has high capital costs (€2000–2500/kW). Photocatalytic and PEC water splitting has lower material costs but remain at the research stage due to low efficiency.

Biological Methods: Fermentation and biophotolysis have moderate costs, but their low yields limit scalability. Gasification and pyrolysis, though commercially feasible, require high capital investment and feedstock preprocessing, which affect economic viability.

4.3. Environmental Impact

Water Splitting: Electrolysis is clean and sustainable when powered by renewable electricity but requires significant energy input. Photocatalysis and PEC methods, while solar-driven and emission-free, still lack efficiency and material stability.

Biological Methods: Biophotolysis and fermentation utilize organic waste, reducing environmental impact. However, gasification and pyrolysis generate tar, CO_2, and other pollutants, making gas cleaning a necessary step.

4.4. Technological Readiness and Future Prospects

Water Splitting: Alkaline and PEM electrolysis are at TRL 9 (commercial stage), with cost reduction strategies focusing on PGM-free catalysts and improved membranes. Photocatalysis and PEC methods are at TRL 4–6, requiring advances in semiconductor materials and charge separation strategies.

Biological Methods: Gasification and pyrolysis are commercially viable (TRL 9), while fermentation and biophotolysis remain in early research stages (TRL 4–6). Genetic modification of microorganisms and reactor optimization are critical for scaling up biohydrogen production.

5. Conclusion

Both water splitting and biological technologies offer promising paths for green hydrogen production, but each comes with trade-offs. Electrolytic water splitting is more efficient and produces high purity hydrogen but requires expensive materials and energy input. Biological methods, particularly gasification and pyrolysis, offer higher yields but involve higher environmental impact and capital costs. Biophotolysis and fermentation, while environmentally friendly, remain technologically immature.

For a sustainable hydrogen economy, a hybrid approach integrating renewable-powered electrolysis, biohydrogen from waste, and novel photocatalysts is essential. Advancements in low-cost catalysts, efficient bioreactors, and material innovations will determine the future competitiveness of these technologies.

Abbreviation

EIF	Environmental Impact Factor
HC	Hydrogen Content Factor
GF	Greanization Factor
OER	Oxygen Evolution Reaction
HER	Hydrogen Evolution Reaction
HHV	High Heating Value
LCOH	Levelized Cost o Hydrogen
PEM	Proton Exchange Membrane
AWE	Alkaline Water Electrolysis
MEA	Membrane Electrode Assembly
GDL	Gas Diffusion Layer
PGM	Platinum Group Metals
IEC	Ion Exchange Capacity
AEM	Anion Exchange Membrane
TRL	Technological Readiness Level
SOWE	Solid Oxide Water Electrolysis
PEC	Photoelectrochemical Cell
ENEA	European Environmental Agency
SCWG	Supercritical Water Gasification
CLG	Chemical Looping Gasification

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Conflicts of Interest

The authors declare no conflicts of interest.

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