

Sustainable Hydrogen Production through Steam Methane Reforming and Water Electrolysis – A Review

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Abstract

Nearly half of the hydrogen produced worldwide comes from the most popular and economical method of hydrogen synthesis, methane steam reforming (MSR). However, there are a number of challenges that must be conquered before MSR can be widely used, despite the fact that it is a well-established technique. The primary research gaps in the MSR process center around improving the catalyst longevity and efficiency, addressing the process's high energy consumption and carbon emissions, and enabling cost-effective small-scale hydrogen production. As an alternative, electrolysis of water could yield pure hydrogen. Nevertheless, hydrogen production from water electrolysis is synonymous with high costs (electricity, capital), as well as obstacles like the synthesis of more affordable and effective catalysts for the procedure, enhancing system intergration with renewables, and achieving true large scale manufacturing and scalability. In this review paper, both processes have been critically analyzed to give insights into current processes, the challenges faced, and prospects. Since both methane steam reforming and water electrolysis generate valuable hydrogen, optimization of the two could offer a more sustainable and reliable source of energy.

Key Words: Green energy, Hydrogen production, Methane reforming, Water electrolysis, Catalytic activity

Introduction

Because its combustion process is carbon-free, hydrogen (H_2) is acknowledged as a feasible and sustainable energy source. The conversion of hydrocarbons into hydrogen has recently been considered as a possible energy source substitute for burning fossil fuels. For example, compared to coal (29 MJ/kg) and fossil oil (42.6 MJ/kg for diesel and 43.4 MJ/kg for petrol), hydrogen has a higher energy content (120 MJ/kg), which gives it a comparative advantage (Hatta et al., 2023). Eco-friendly hydrogen gas and oxygen are produced when water is electrolysed utilising renewable energy sources like solar or wind

power. However, green H_2 contributes to a small fraction of the H_2 in industry because its production is expensive. On the other hand, methane steam reforming (MSR) combines natural gas with steam to make blue H_2 , with CO_2 as an undesired byproduct. Fortunately, blue H_2 , which is sometimes referred to as 'low-carbon H_2 ', incorporates a carbon capture and storage (CCS) mechanism. Grey H_2 , which is the most common form of H_2 , is simply blue H_2 , without a CCS system (Saha et al., 2024).

Currently, the reforming of CH_4 into H_2 is the most viable when considering resource availability and process-associated costs. Yet,

with carbon emissions, this option is deemed to be environmentally unattractive and unsustainable (Arutyunov et al., 2022). In an ideal world, carbon-free hydrogen production could be achieved using water electrolysis. An electrolyte separates the anode and cathode of an electrolyzer, much like in a fuel cell. How electrolyzers function depends on the different electrolyte materials and ionic species utilised in their fabrication (Kumar & Lim, 2022). In this review, both carbon-related (methane reforming) and carbon-free (water electrolysis) methods of

Figure 1 depicts the type of H₂ production methods that make use of fossil fuels and are accomplished by reforming hydrocarbons. CH₄,

H₂ production are analyzed, with the aim of giving insights into the current production methods, their accompanying challenges, and perspectives.

H₂ Production through CH₄ Reforming

The four main sources of H₂ produced commercially today are oil, coal, natural gas, and electrolysis. About 30%, 18%, 48%, and 4% of the world's H₂ production comes from these four sources, respectively (Marzouk, 2024).

which is present in natural gas, may be used to produce H₂ through thermal processes like steam and dry reforming.

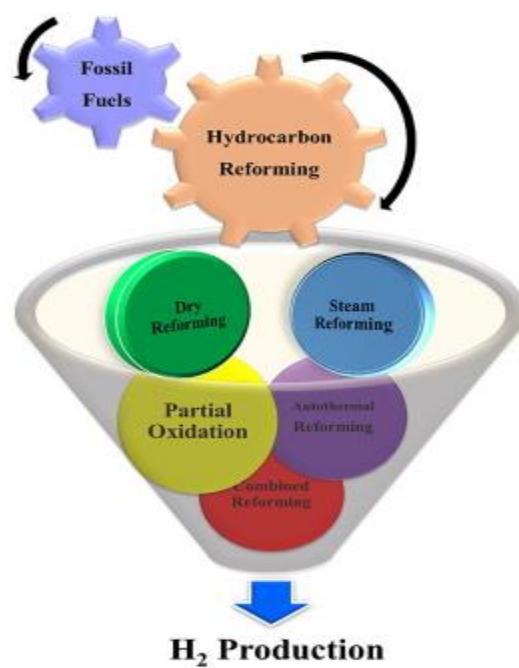


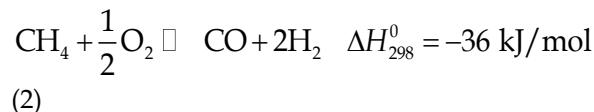
Figure 1. H₂ production processes from fossil fuels

The synthesis of H₂ through the reforming of CH₄ can occur via a variety of distinct pathways. This is mostly dependent on the reactant species (CO₂/ O₂/ H₂O) that drives the formation of products, and the processes that correspond to them are dry, partial, and steam methane reforming, respectively. Methane dry reforming (MDR) uses CO₂ as an oxidiser to produce H₂ as per Eq. (1).



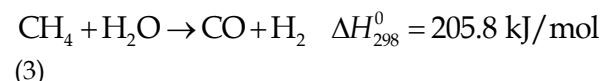
Despite producing valuable H₂, MDR is a very endothermic reaction that requires a large amount of energy. Furthermore, the creation of coke/ carbon regrettably leads to the deactivation of conventional catalysts that are based on nickel. It is also important to consider the requirement for pure carbon dioxide in the feed mixture, which can be met by a limited number of production methods, such as gasification and fermentation (Lavoie, 2014).

Methane partial oxidation (MPO) can be used in the methane reforming process to lessen the energy requirement. As can be seen in Eq. (2), the reaction is spontaneous, exothermic, and can initiate in the absence of a catalyst.



When the MPO reaction is homogeneous, high operating temperatures of between 1100 and 1500 °C are required. CO generation also necessitates

a gas separation device, which drives up installed capital costs significantly (Council & Engineering, 2004). On the contrary, MSR occurs through Eq. (3), as follows:



Methane steam reforming (MSR) is currently the most advanced method for producing hydrogen in general as well as for turning CH_4 into H_2 (Figure 2) (Boretti & Banik, 2021).

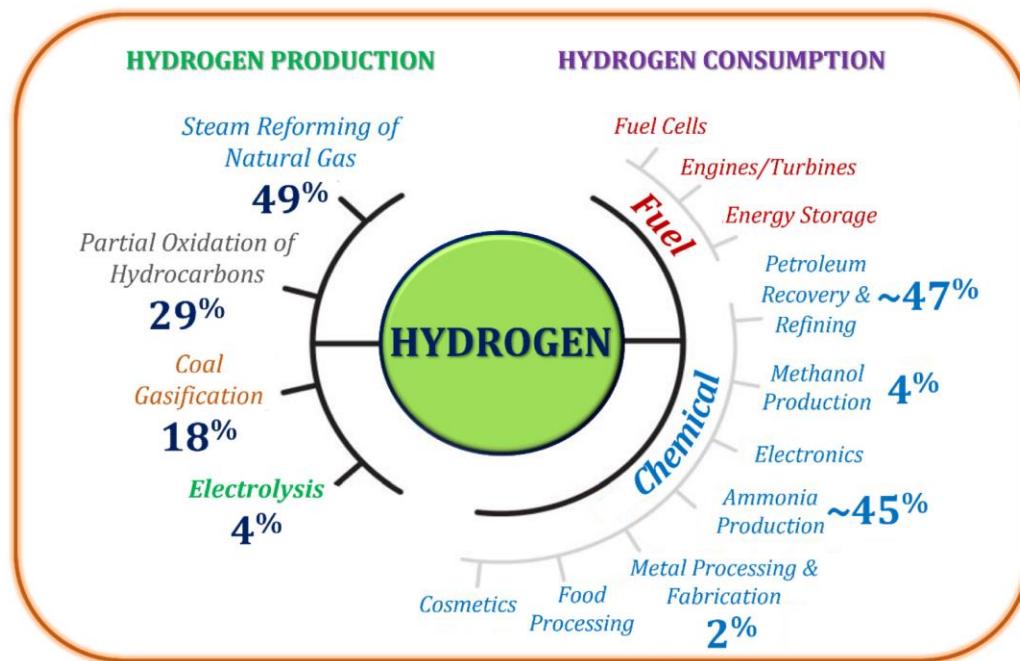
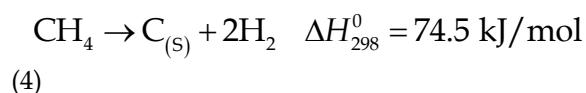


Figure 2. Hydrogen production processes versus consumption outlets

Temperatures between 700 °C and 900 °C are necessary for a constant conversion in the highly endothermic MSR process. In addition, MSR is enhanced by low-pressure conditions and catalysis. Regrettably, the MSR process is susceptible to catalyst deactivation, which arises from carbon deposition. Carbon is formed in two ways: from CH_4 decomposition (Eq. (4)) and the Boudouard reaction (Eq. (5)) (Schulz et al., 2015).



(5)

In MSR, nickel is frequently used as an active metal for catalysis because it strikes an optimal balance between thermochemical performance and cost. Meanwhile, particles of alumina (Al_2O_3) serve as support (Yoo et al., 2015). MSR is typically followed by a process known as water-gas shift (WGS) reaction (Eq. (6)). WGS has two purposes: first, it reduces the amount of carbon monoxide, and second, it speeds up the production rate of hydrogen.

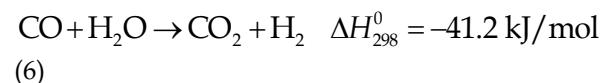


Figure 3 illustrates the fundamental steps involved in MSR. Initially, CH_4 is steam-reformed into synthesis gas (H_2/CO). The

synthesis gas is then reacted in one or more shift converters, creating more H_2 in the process. Finally, the H_2 gas is purified by CO_2 removal, methanation, and cooling (Rosen, 1991).

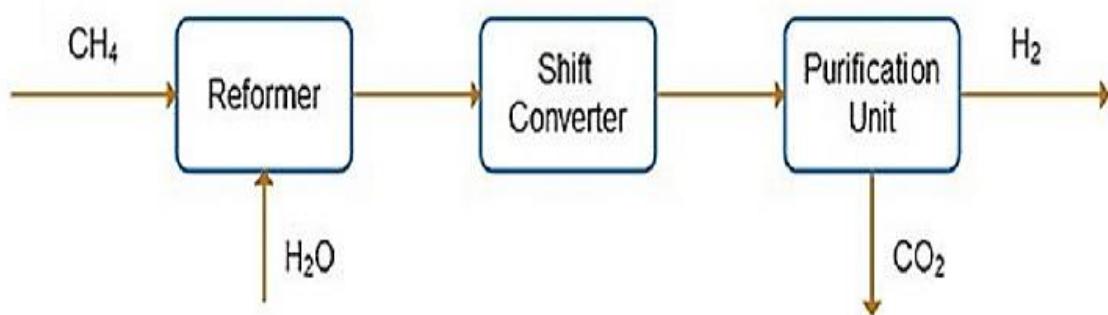


Figure 3. Simplified process flowsheet for H_2 production via MSR (Rosen, 1991)

Catalysis of MSR

As shown in

Figure 4, several variables such as feed molar ratio, temperature, and pressure affect the product distribution of the MSR process. These parameters include: the feed molar ratio, which is the relation between the amount of methane and

water (steam) in the feed mixture, temperature, and pressure of the reaction mixture.

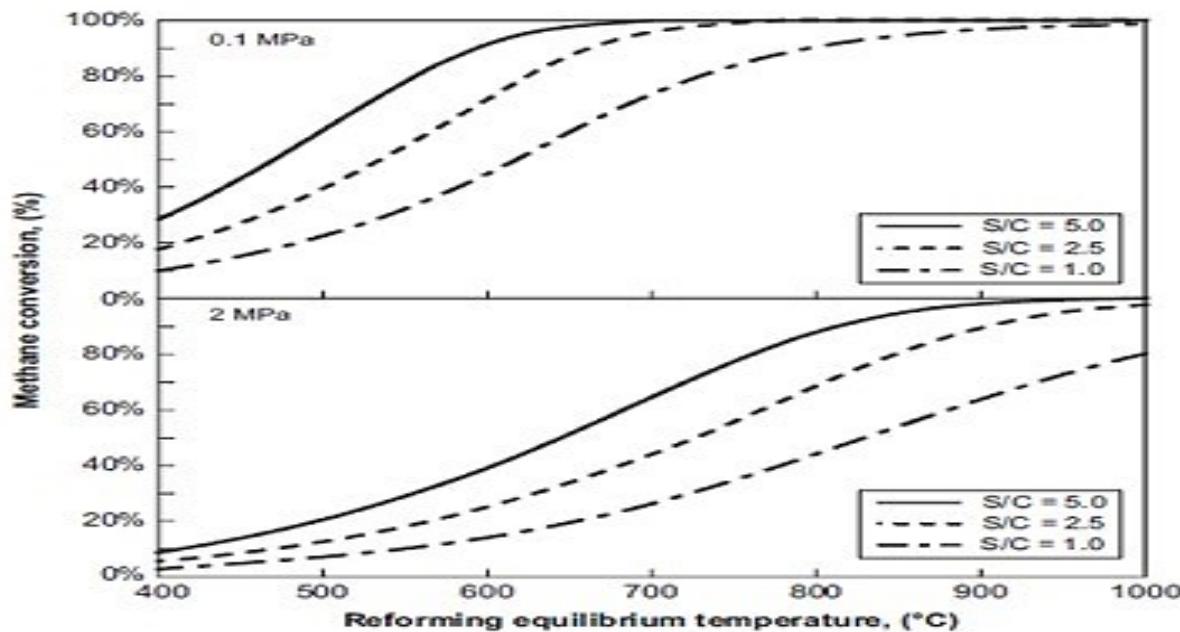


Figure 4. CH_4 Conversion at Different Feed Molar Ratios, Temperature, and Pressure (Rostrup-Nielsen & Christiansen, 2011)

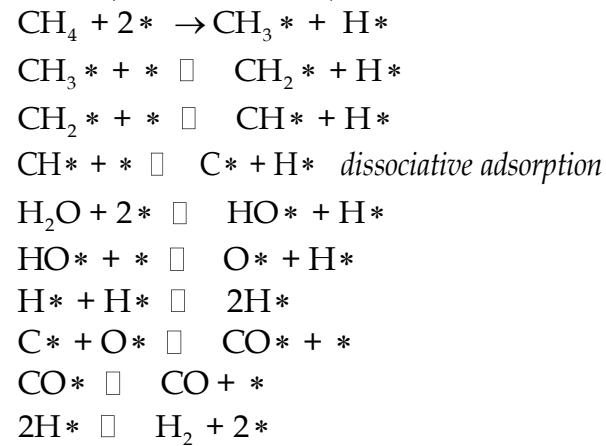
Methane conversion is best with a high steam-to-methane ratio, low pressure, and high temperatures, but can be further enhanced through catalysis (Rostrup-Nielsen & Christiansen, 2011). With catalysis, high conversions could also be attained at much lower temperatures, which would reduce the energy costs of the MSR process. In addition, catalysis would promote product selectivity, where H_2 would be favoured over CO or CO_2 production. Although late transition metals like Pd, Pt, Ru, Rh, and Ir can be used as catalysts for steam reforming, nickel-based catalysts are the most economically feasible choice. Even though they are active, reactive metals like iron and cobalt are vulnerable to oxidation under process conditions. While ruthenium, rhodium, and other noble metals are more active than nickel, they are also more costly (Chorkendorff & Niemantsverdriet, 2017). For catalyst supports to withstand steam pressures exceeding 3 MPa and temperatures beyond 800 °C without failing, mechanical stability is of the utmost importance.

Additionally, it is crucial that the support be free of any volatile substances. γ -alumina and chromium are examples of high-area supports that could be used for low-temperature adiabatic reforming catalysts. However, as the temperature exceeds 500 °C, these supports undergo considerable sintering and weakening. Because of its flammability in high-pressure steam, silica is not typically employed as a catalyst in steam reforming processes unless combined with an alkali (Taifan & Baltrusaitis, 2017). Most recently,

the challenge of desulfurizing heavy feedstock in the petroleum industry has led to the adoption of non-metallic catalysts in steam reforming. Unfortunately, non-metal catalysts are far less active (Wang et al., 2023).

Mechanism of the MSR Process

Methane is a highly symmetrical and stable compound. Direct dissociative adsorption activates it, raising energy and entropy barriers. Steam reforming's rate-limiting step is the dissociative adsorption, which makes sense given methane's extremely low sticking coefficients. The overall reaction scheme is as follows (Richter et al., 2023):



Depending on the surface, the energy diagram shown in Figure 5 reveals that the most stable intermediates are C or CH species. On the ideal (111), CO dissociation favours the methanation reaction, whereas on the stepped (211), it presents a significant barrier. As a result, it is hypothesized that the places where CO dissociates are steps on the (111) surface.

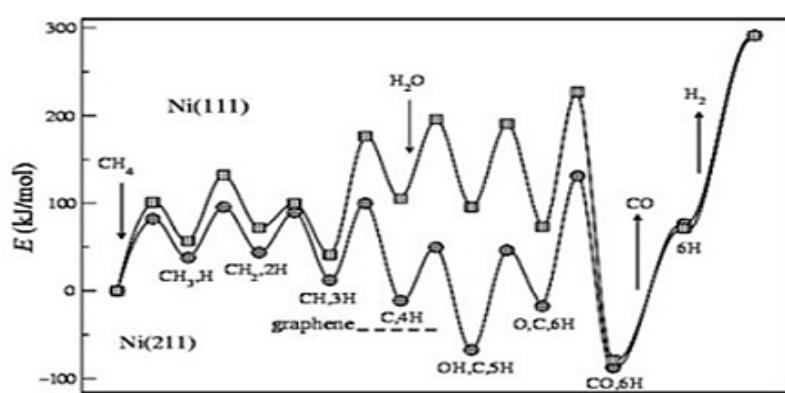


Figure 5. Energy Diagram for Methane Steam Reforming (Bengaard et al., 2002)

Challenges in the MSR Process

Methane steam reforming has a well-established process technique and produces the most H₂. Yet, the highly endothermic reaction and steady heat supply requirement increase the heat load, which is a drawback. During the reaction, catalyst sulphur poisoning and coke deposition cause mass and heat transfer difficulties. Among the group VIII metals, nickel is the most susceptible to sulphur poisoning. Two-dimensional sulfides

The nickel steam-reforming catalyst is strong yet also vulnerable to carbon deposition (Lee, 2013). As indicated in Figure 6, carbon (C) can build on the catalyst from several reactions. Carbon production increases with decreased oxidation potential, or steam content. Carbon and fractured catalyst pellets may cause feed misdistribution and reformer tube overheating, affecting tubular reactor operation. Avoiding thermodynamic

nicely characterize the H₂S/Ni system (Ib et al., 1981). The H₂O/H₂ ratio does not affect sulphur coverage. Chemisorption is reversible, but desorption is usually weak. Sulphur poisoning is less common with noble metal catalytic partial oxidation (CPOX). Oxygen oxidizes sulphur to SO₂, which the catalyst does not adsorb. Nickel oxidizes with oxygen, but the CPOX catalyst rhodium does not. The presence of oxygen is necessary for the activity of rhodium. Following the depletion of O₂, SO₂ will undergo a transformation into H₂S and be chemisorbed onto the catalyst.

zones with carbon deposition is one of the methods that has been employed to mitigate the carbon issue. However, due to radial and especially vertical changes in reactor temperature and gas composition, this severely restricts the parameter space. Therefore, a catalyst that is far more resistant to carbon deposition than the typical catalysts used in steam reforming is required.

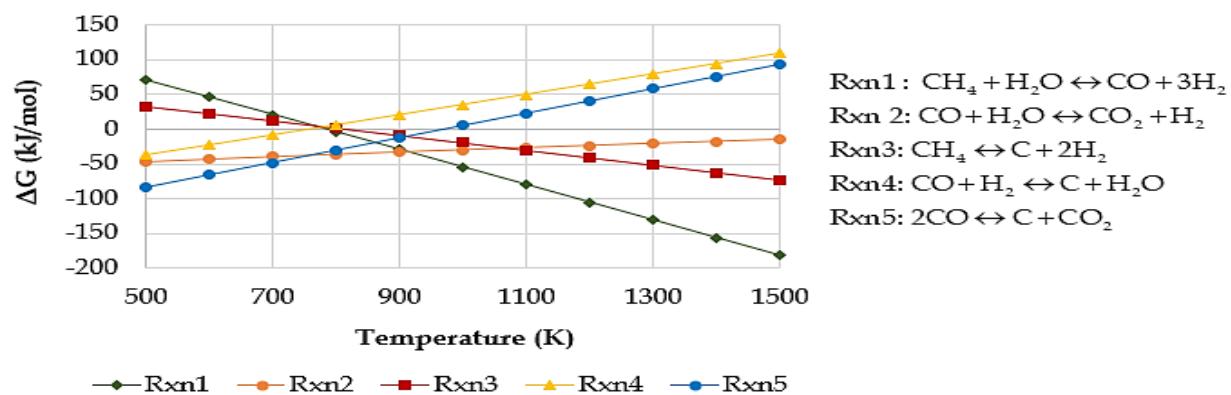


Figure 6. Gibbs Free Energy Change for MSR and Associated Side Reactions (Farshchi Tabrizi et al., 2015)

H₂ Production from Water Electrolysis

Electrolysis, which breaks down water into its constituent parts using electricity, is one method

of producing H₂ gas. This technique is particularly noteworthy as an eco-friendly way to produce H₂ when the electricity is generated using renewable energy. The process is conducted in an electrolyzer as illustrated in Figure 7.

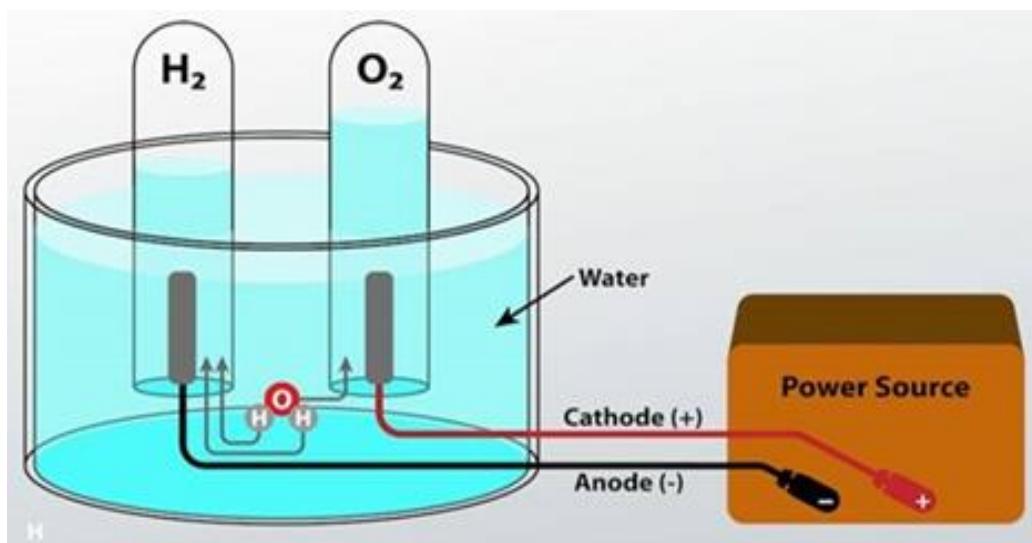


Figure. 7 Water Electrolysis Apparatus

The anode water molecules oxidize and release O_2 gas, protons, and electrons when an electric current passes through them during electrolysis. Protons move through the electrolyte to the cathode, where they acquire electrons and transform into H_2 gas. Powered by electricity, the chemical reaction is endothermic. Catalysts lower the energy barrier for reactions at both electrodes, which improves the electrolysis efficiency (Wang et al., 2021). Electrolyzer and catalyst selection depend on system operating conditions, hydrogen purity, and efficiency. Proton exchange membrane (PEM) (Wang et al., 2022), alkaline (Brauns & Turek, 2020), and solid oxide electrolyzer cells (Hauch et al., 2020) are the primary types of Electrolyzers. Electrolysis-produced H_2 can replace fossil fuels in transportation, industry, and heating, helping the world reach net-zero emissions.

Reaction Mechanisms of Water Electrolysis

Water electrolysis at the anode and cathode is dominated by oxidation and reduction reactions. The electric potential causes oxidation at the anode. This procedure makes use of the oxygen evolution reaction (OER) catalyst. H_2O molecules are oxidized to form O_2 gas in this multistep mechanism (Li et al., 2019). H_2O molecules adsorb onto the catalytic surface to start the process. Once adsorbed, the catalyst weakens H_2O molecules' O-H bonds, releasing O atoms for reaction. Next, the catalyst helps remove H^+ ions (protons) from H_2O molecules. This critical phase

generates free electrons and protons. The anode sends electrons out into the circuit, and the electrolyte receives protons. The catalyst pairs oxygen atoms by overcoming their resistance to form an oxygen-oxygen bond, producing molecular O_2 . This phase is crucial because O_2 molecule production is less energetically favoured without the catalyst. The newly produced O_2 molecules desorb from the catalyst and bubble away as gas.

Reducing H^+ ions at the cathode produces H_2 gas from H_2O in a process called the hydrogen evolution reaction (HER) (Wu et al., 2021). H^+ ions (protons) in the electrolyte or H_2O molecules in alkaline solutions receive electrons from the cathode to start this process. Electrons from the external electrical circuit are necessary for reduction. With electrons, protons become H atoms, which are extremely reactive and easily form diatomic hydrogen molecules (H_2). The mechanism begins with the adsorption phase. Once bound, the adsorbed species gain electrons from the cathode and are reduced. In the case of protons, this results in the formation of atomic hydrogen, which quickly pairs up to form H_2 molecules. As summarized in Table 1, in an alkaline medium, H_2O molecules gain electrons to form OH^- ions and H atoms, which then also pair up to form H_2 gas. The H_2 gas molecules then desorb from the catalyst surface.

Table 1. Anode-Cathode reactions of H_2O electrolysis
(Smolinka, 2009)

Medium	Anode	Cathode
Acidic	$\text{H}_2\text{O} + * \rightleftharpoons \text{H}_2\text{O}^*$ $2\text{H}_2\text{O}^* + 4* \rightarrow 4\text{H}^{+*} + \text{O}_2^* + 4\text{e}^-$ $\text{H}^{+*} \rightleftharpoons \text{H}^+ + *$ $\text{O}_2^* \rightleftharpoons \text{O}_2 + *$	$\text{H}^+ + * \rightleftharpoons \text{H}^{+*}$ $2\text{H}^{+*} + 2\text{e}^- \rightarrow \text{H}_2^* + *$ $\text{H}_2^* \rightleftharpoons \text{H}_2 + *$
Basic/ Alkaline	$\text{OH}^- + * \rightleftharpoons \text{OH}^{-*}$ $4\text{OH}^{-*} + 4* \rightarrow 2\text{H}_2\text{O}^* + \text{O}_2^* + 4\text{e}^-$ $\text{H}_2\text{O}^* \rightleftharpoons \text{H}_2\text{O} + *$ $\text{O}_2^* \rightleftharpoons \text{O}_2 + *$	$\text{H}_2\text{O} + * \rightleftharpoons \text{H}_2\text{O}^*$ $2\text{H}_2\text{O}^* + 2\text{e}^- + * \rightarrow 2\text{OH}^{-*} + \text{H}_2^*$ $\text{OH}^- + * \rightleftharpoons \text{OH}^{-*}$ $\text{H}_2^* \rightleftharpoons \text{H}_2 + *$

Electrolyzers

Electrolyzers are crucial for H_2 generation. They split H_2O into H_2 and O_2 . Based on their electrolyte and operational qualities, these systems vary in efficiency, cost, and applicability. Electrolyzer technologies (

) offer many H_2 generation possibilities, each having pros and downsides that must be addressed when integrating into the energy grid (Anwar et al., 2021). Alkaline Electrolyzers use potassium or sodium hydroxide electrolyte solutions. To stop gas mixing but permit ion flow,

an anode and a cathode are immersed in the electrolyte solution and kept apart by a diaphragm. H_2O at the cathode becomes H_2 gas and OH^- ions when electricity is supplied. The electrolyte transports OH^- ions to the anode, where they oxidize to form O_2 and H_2O , completing the circuit. Alkaline Electrolyzers are durable and are efficient at 60°C to 90°C and have high current densities, making them suited for large-scale H_2 generation (Kovač et al., 2019). Despite that, their application of caustic electrolytes requires careful material selection and maintenance to prevent corrosion and guarantee long-term functioning.

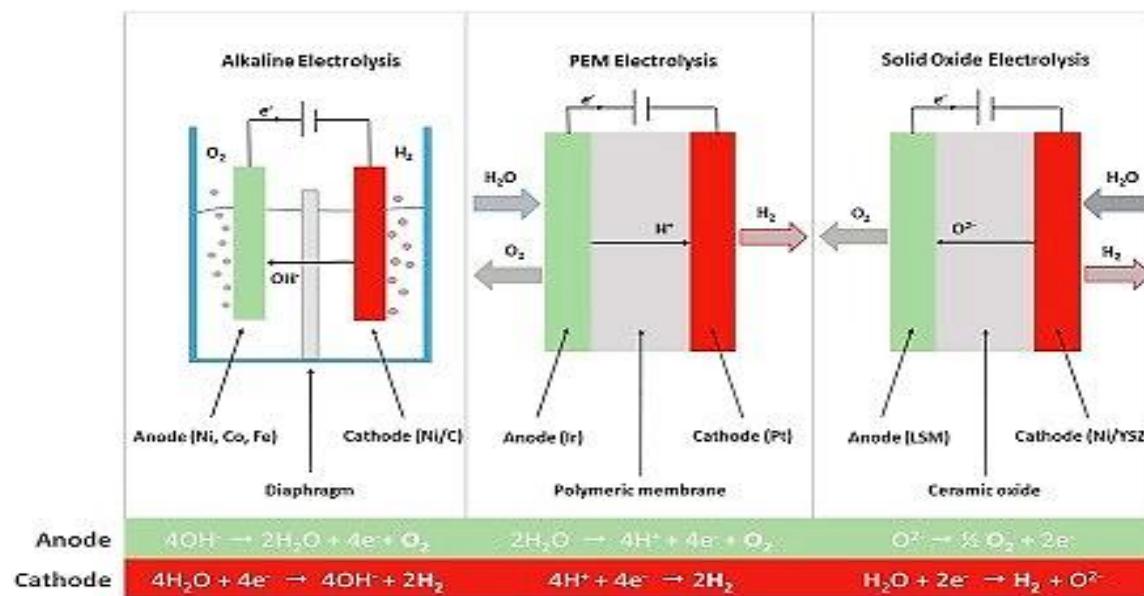


Figure 8. Operation Principles of Different Electrolyzers (Sapountzi et al., 2017)

Only protons can pass through the electrolyte, a solid polymer membrane, in Proton Exchange Membrane (PEM) Electrolyzers, while electrons must go around an external circuit to produce current (Kumar & Himabindu, 2019). This allows a compact design and fast start-up, making it extremely adaptable to electrical input changes. This function is useful when integrating renewable energy sources with variable power outputs, like solar or wind. Running at 50 to 80 °C, PEM Electrolyzers create high-purity H_2

efficiently, making them popular. Water oxidation at the anode generates protons and oxygen gas in the membrane-electrode assembly, the system's heart. The protons pass the membrane and unite with electrons to generate hydrogen gas at the cathode. The electrodes are coated with platinum and iridium catalysts, which are effective but make PEM systems more expensive than other Electrolyzers.

Solid oxide electrolyzer cells (SOECs) are high-temperature Electrolyzers that use solid ceramic electrolytes. Zirconium oxide stabilized with yttrium oxide conducts oxygen ions at 700 to 800 °C in the ceramic (Milewski et al., 2021). SOECs' high working temperature reduces the electrical energy needed to break water molecules, but it also poses material and system durability issues. Steam is utilized as a feedstock in SOECs to improve electrolysis thermodynamics due to the high temperature. The SOEC converts cathode steam to H₂ gas and oxygen ions when a voltage is supplied. After passing through the solid electrolyte, the oxygen ions are released at the anode as O₂ gas. SOECs outperform standard Electrolyzers due to their better reaction kinetics at high temperatures (Liu et al., 2021).

Catalysis of Water Electrolysis to H₂

Alkaline Electrolyzers need nickel-based catalysts. They catalyze the H₂ evolution process (HER) in high-pH conditions and are cheaper than precious metals. Pure nickel's catalytic characteristics make it a reliable catalyst in these conditions. Nickel electrodes are robust and active in alkaline mediums, reducing H₂O to H₂ electrochemically (Angeles-Olvera et al., 2022). Nickel catalyst effects improve when alloyed with other metals. Nickel-molybdenum (Ni-Mo) and nickel-iron (Ni-Fe) alloys demonstrate increased catalytic activity and stability. Nickel-based oxides and hydroxides are also used in alkaline Electrolyzers for the O₂ evolution reaction (OER). The catalytic characteristics of platinum group metals (PGMs) make them valuable in hydrogen generation (Ming et al., 2019). PGMs contain platinum, palladium, iridium, and ruthenium. Platinum is very useful in Proton Exchange Membrane (PEM) Electrolyzers for the H₂ evolution reaction (HER). However, PGMs are expensive and scarce,

limiting their utilization and raising electrolyzer system costs (Salonen et al., 2021).

Challenges to Electrolyzer Performance

PEM water electrolysis cells use platinum (Pt) as a catalyst due to its excellent catalytic characteristics towards the H₂ evolution reaction and good electrical conductivity, which helps electron transport during catalysis. Pt's surface chemistry optimizes hydrogen atom adsorption and desorption during the HER intermediary stages. Smaller, well-dispersed Pt nanoparticles increase the reaction surface area and catalytic efficiency. However, smaller particles may be less stable and more likely to aggregate, reducing their effectiveness. Another important aspect is the Pt loading on the catalyst. Pt is expensive; thus, optimal loading maximizes catalytic activity while minimizing expenses. Too little Pt may not provide enough catalytic sites for efficient reaction rates, while too much may be economically prohibitive and reduce performance. Stability is also crucial to platinum catalyst performance. Sintering and corrosion can degrade Pt catalysts over time. Using Pt in PEM cells requires balancing between activity and long-term stability.

Platinum catalyst deactivation in electrolysis is a major issue that affects system efficiency and longevity. Sintering, corrosion, and poisoning cause deactivation. Platinum particles sinter thermally, reducing the catalyst's active surface area and activity. Platinum atoms move more at high operating temperatures, forming larger, less reactive clusters. Another prominent source of deactivation is catalyst corrosion, especially carbon-supported platinum catalysts. Carbon corrosion in electrolytic settings, especially at high potentials, can detach and lose platinum particles. While reducing active platinum, this can contaminate the electrolyte and other system components. Adsorption of electrolyte or feedstock contaminants poisons platinum surfaces. Sulphur compounds, carbon monoxide, and chloride ions can aggressively adsorb onto platinum surfaces, blocking active sites and impeding electrolytic reactant adsorption. Poisoning relies on impurity concentration and electrolysis system operation.

Maintaining platinum catalyst efficiency and longevity in electrolysis systems requires preventing deactivation. **Enhancing Thermal Stability:** Thermal stability can be improved in catalysts to prevent sintering, which aggregates platinum particles. Platinum is alloyed with other metals to stabilize particle size and prevent agglomeration. When alloyed with platinum, ruthenium, iridium, or cobalt can preserve platinum nanoparticle dispersion at high temperatures. For carbon-supported platinum catalysts, catalyst support corrosion is a major cause of deactivation. More corrosion-resistant supports, like metal oxides or conductive polymers, can help. These materials degrade less in the electrolytic environment, stabilizing platinum particles. Purifying feedstocks and electrolytes to eliminate sulphur compounds, carbon monoxide, and chloride ions reduces impurity poisoning. Structural or protective layer alterations to the platinum surface can help reduce toxicity. Optimal electrolysis system operation extends platinum catalyst life. This includes maintaining proper temperature and voltage ranges to prevent thermal degradation and electrochemical corrosion. Developing platinum catalyst regeneration technologies is another option. Chemical or thermal treatments may eliminate deposited toxins or redistribute platinum particles on the support.

Conclusion and Recommendations

Methane and other hydrocarbons can be successfully reformed in industrial settings using steam. The future of methane steam reforming (MSR) lies in its evolution into low-carbon "blue" (hydrogen produced from methane using steam reforming, but with the resulting CO₂ captured and stored underground (Carbon Capture and Storage - CCS)) and even "turquoise" (low-carbon hydrogen produced from methane using methane pyrolysis, a process that splits methane into hydrogen gas and solid carbon) hydrogen, driven by advanced catalysts, electrification (eMSR), and integration with carbon capture (CCS)/utilization (CCU), making it a vital bridge technology for decarbonizing industry and energy, despite conventional MSR's high emissions. Key prospects include more efficient, modular plants, using renewable electricity for heating, and hybrid systems (like SE-MSR,

sorption enhanced methane steam reforming) that combine reforming with in-situ CO₂ capture, significantly cutting costs and emissions while leveraging MSR's proven large-scale capabilities for the growing hydrogen economy.

On the other hand, renewable energy makes water electrolysis and hydrogen production eco-friendly. This method requires Electrolyzers, which are alkaline, PEM, and SOECs. The future of water electrolysis for H₂ production looks strong, driven by net-zero goals, with significant growth expected as technology improves and costs drop, especially with cheap renewables. Platinum-based hydrogen generation catalysts are effective but expensive and scarce. Additionally, we must handle platinum catalyst deactivation from sintering, corrosion, and poisoning. Alloying and corrosion-resistant supports, purifying feedstocks, optimizing operational conditions, and inventing catalyst regeneration methods to increase efficiency and longevity could prevent this. Platinum is essential for electrolysis-based hydrogen production, but its limitations require continual research and innovation. H₂ will be essential to a clean, sustainable energy future if materials science, catalyst design, and system integration improve.

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