

A Review of the Recent Advances in Composite Membranes for Hydrogen Generation Technologies

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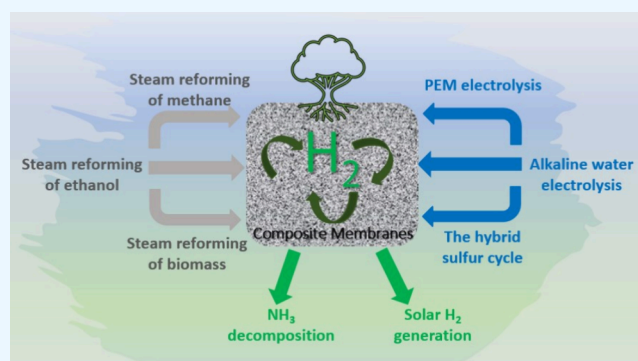
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ABSTRACT: Keeping global warming at 2 degrees and below as stated in the “Paris Climate Agreement” and minimizing emissions can only be achieved by establishing a hydrogen (H_2) ecosystem. Therefore, H_2 technologies stand out in terms of accomplishing zero net emissions. Although H_2 is the most abundant element in the known universe, molecular H_2 is very rare in nature and must be produced. In H_2 production, reforming natural gas and renewable hydrogen processes using electrolyzers comes to the fore. The key to all these technologies is to enhance production speed, performance, and system lifetime. At this point, composite membranes used in both processes come to the fore. This review article summarizes composite membrane technologies used in methane, ethanol, and biomass steam reforming processes, proton exchange membranes, alkaline water electrolysis, and hybrid sulfur cycle. In addition to these common H_2 production technologies at large quantities, the innovative systems developed with solar energy integration for H_2 generation were linked to composite membrane utilization. This study aimed to draw attention to the importance of composite membranes in H_2 production. It aims to prepare a guiding summary for those working on membranes by combining the latest and cutting-edge studies on this subject.



1. INTRODUCTION

Current natural disasters triggered by climate change, which is a main result of excessive carbon dioxide (CO_2) emissions, have compelled a great number of countries to commit to achieving net zero emissions by 2050.^{1,2} However, the net zero emission goal by the targeting period requires urgent actions in the energy and economy sectors. For this purpose, a concrete step was taken with the “Kyoto Protocol” which was signed with the gathering of 183 countries in 1997, and the “Paris Agreement” at the Paris Climate Change Conference in 2015. Resultingly, the Paris Agreement denoted a long-term global temperature target below 2 °C. To date, research and developments have accelerated the utilization of sustainable clean energy to attain a promising solution.

Hydrogen (H_2) is regarded as one of the most sustainable energy carriers since it releases more energy without emitting CO_2 as compared to fossil fuels. Besides, it can be produced from many technologies that involve renewables.^{3–7} Additionally, the storage and transportation of H_2 are more convenient than those of nonrenewable energy sources.^{8–11} Therefore, the worldwide prominence of H_2 as well as the investments in the production and utilization have been accelerated by 40 countries since 2022.¹ The H_2 production technologies can be categorized into two main groups based on resources

renewable and nonrenewable. These technologies are labeled according to the association with greenhouse gas emissions; conventional, low- CO_2 or CO_2 -free, and carbon-free production routes. The resulting H_2 is often expressed by the color descriptions such as “gray”, “blue”, “turquoise”, and “green”. Currently, industrial-scale H_2 production rely on 48% of methane reforming, 30% of oil/naphtha reforming in refineries or chemical industries, 18% of coal gasification, 3.9% of electrolysis of water, and 0.1% of other sources.¹² This means that the major H_2 production is from gasification and reforming of nonrenewable carbon-based sources. However, the use of renewable energy for “green hydrogen” production is consciously increasing in most countries to attain a quick recovery of the damages caused by excess CO_2 emission. Green H_2 is produced by the electrolysis of water which is the process of converting water into H_2 and O_2 in electrolyzers using renewable energy.

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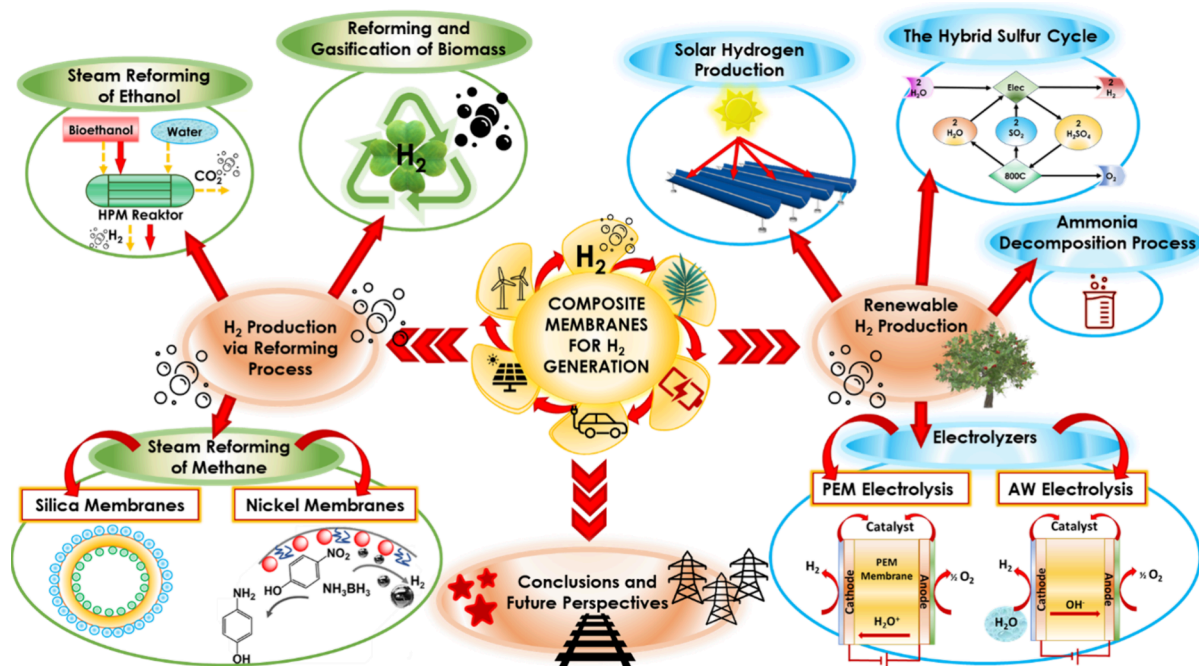


Figure 1. Main H_2 production processes that involve composite membranes; from reforming processes to renewable H_2 production (reproduced with permission from refs 20–23, Copyright 2021 MDPI, Copyright 2023 American Chemical Society, Copyright 2017 Elsevier B.V.).

Membranes are of the essence in H_2 technologies as they directly affect the efficiency and lifetime of the system. Membranes, which are classified as either inorganic or organic membranes, act as a physical fence allowing a selective passage of the species. Organic membranes can have either polymeric or biological components, while inorganic membranes are metallic and ceramic. Inorganic membranes have higher mechanical and thermal resistance than organic membranes.¹³ Metallic membranes are made of metals such as palladium (Pd), platinum (Pt), nickel (Ni), titanium (Ti), copper (Cu), aluminum (Al), and stainless steel (SS). Composite membranes, however, may contain polymers, metals, and ceramics.¹⁴ Composite membranes combine at least two different materials, providing superior properties to each component, such as enhanced selectivity and high permeability.¹⁵ Their properties may vary depending on the application areas and the components they contain. Standard membranes which are prepared from aromatic polymers in general exhibit better proton conductivity due to the higher degree of sulfonation. Unfortunately, the higher degree of sulfonation, at the same time, hurts the mechanical strength as it leads to swelling of the polymer in water due to the higher solubility. In addition, especially for industrial applications, meeting crucial requirements such as high durability and enhanced performance as well as high gas purity is necessary. However, the physical and electrochemical assets of the membrane can be enhanced by forming composites that contain either polymer composites or both organic and inorganic compounds.^{16–19}

This review focuses on the recent progress of composite membranes in various hydrogen production technologies (as schematically summarized in Figure 1).^{20–22} As mentioned above, the most common industrial H_2 production process is steam-reforming of natural gas. Therefore, we primarily focus on the composite membranes used in reforming processes. Later, the H_2 production through water electrolysis processes

in alkaline water (AW), polymer electrolyte membrane (PEM), and hybrid sulfur electrolyzers utilizing composite membranes is reviewed. Ammonia (NH_3) decomposition in membrane reactors is a rising interest in the H_2 energy research area due to the high hydrogen content of NH_3 . Catalytic membrane reactors as H_2 -selective membrane systems are widely used systems in the NH_3 decomposition process. Thus, the advantages of composite membranes in membrane reactors are summarized for the NH_3 decomposition process. Finally, the use of solar energy, the most powerful renewable energy source, for H_2 production using composite membranes is reviewed. The solar H_2 production systems can be achieved by two different routes: water electrolysis powered by solar-generated electricity and direct solar water splitting from photocatalytic/photoelectrochemical processes.

2. COMPOSITE MEMBRANES FOR H_2 PRODUCTION VIA REFORMING PROCESS

2.1. Steam Reforming of Methane and Natural Gas.

Steam reforming of methane is one of the most widely used methods for manufacturing H_2 and contributes the almost 48% of global H_2 production.^{24–26} On an industrial scale, this reaction is carried out conventionally to form a stream of very pure H_2 but the operation temperature is very high (typically at 800–900 °C). The syngas produced from the conventional steam reforming of methane contains 70–72% H_2 , 10–14% CO_2 , 8–10% CO , and 6–8% CH_4 .²⁷ However, H_2 gas high-purity is required for many applications such as PEM fuel cells. Even a small impurity (such as a CO concentration greater than 10 ppm) initiates the poisoning of the catalyst. Therefore, some complicated processes including reforming streams via water gas shift (WGS) reactors, pressure swing adsorption, and other purification devices are used to decrease the CO concentration. Membrane reactors containing an H_2 permeable membrane that enables more efficient chemical reaction, as a potential alternative solution to this complexity,

were developed to obtain high purity H₂.^{28,29} The system also allows methane steam reforming reactions to be performed under more tolerant operating conditions than those that are necessary for conventional reactors.

2.1.1. Silica Membranes. Alumina, silica, and zirconia are the most common ceramic membranes for hydrogen production from the reforming process. Among all, microporous silica comes to the fore due to its significant potential in hydrogen separation at high operating temperatures and durability in chemically destructive medium and high hydrogen permeation characteristics.³⁰ Although the measured H₂ selectivity is low, the flux or throughput is relatively high, and a cascade of composite silica membrane is an attractive option for concentrating hydrogen for commercial use including fuel cells. The effect of temperature on the permeance does not support either an activated or adsorptive transport mechanism due to the relatively low correlation coefficient. Amanipour et al. created an H₂-selective nanocomposite ceramic membrane by depositing a thick layer of SiO₂ and Al₂O₃ on a graded multilayer substrate.³¹ H₂ passed through the membrane selectively. After 6 h of deposition, H₂ permeance flow decreased from $5 \times 10^{-5} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ for a new substrate to 6.30×10^{-7} , whereas H₂ selectivity over N₂ increased from 5.6 to 203. They also showed using Dynamic light scattering (DLS) analysis that lowering hydrolysis time and increasing acid concentration reduced boehmite sol particle size in the range of 50–700 nm. Longer hydrolysis time and lower acid content resulted in greater sol particle size, which was thought to be associated with sol agglomerates. Scanning electron microscope (SEM) scans of the membrane cross-section revealed a multilayer structure with a 2.5 μm intermediate thickness and 80–100 nm top selective layer. In the dense top layer, gas permeation switches from Knudsen diffusion in the intermediate layer to stimulated hopping between solubility sites. Akbari et al. prepared hydrogen-selective and hydrothermally stable membranes.³² In steam methane reforming, the composite membrane purified H₂ from the synthesis gas. Silica-zirconia layer was deposited by the chemical vapor deposition (CVD) process at 923 K and atmospheric pressure, while the alumina base layer was prepared via the sol-gel method. The composite membrane improved H₂ selectivity over other gases. H₂/CH₄, H₂/CO, and H₂/CO₂ selectivity rose from 700, 350, and 70 in 5 h to 1600, 750, and 570 in 12 h by utilization of CVD deposited membrane. The silica-zirconia membrane changed gas permeability from H₂ > CH₄ > CO₂ > CO to H₂ > CO₂ > CO > CH₄, improving product-methane feed separation. Finally, the hydrothermal stability test showed that the CVD deposited silica-zirconia membrane for H₂ lost 45.7% permeability after 48 h, whereas modified alumina CVD lost as much as 92.5%.

Lawal et al. studied carbonized ceramics extensively.^{33–35} Hydrothermal H₂ production may benefit from carbonized ceramic membranes. The amorphous carbon nanoparticles that formed inhibited the silanol (–Si–OH) migration and condensation that resulted in the closure of the microporous structure. In addition to this, the presence of the carbon nanoparticles also served to increase the pore volume required for enhanced H₂ permeability.^{33,34,36} However, the surfactant carbonization route did not allow pore size tuning of the silica structure for targeted applications.³⁷ Composite carbon-SiO₂–ZrO₂ membranes were tested for long-term hydrothermal performance. A carbon–SiO₂–ZrO₂ composite was generated

by inert pyrolysis of polybenzoxazine resin. The surface and microstructure of carbon–SiO₂–ZrO₂ composites produced at 550 and 750 °C differed. A 750 °C carbon–SiO₂–ZrO₂ membrane had H₂ selectivity over CO₂, N₂, and CH₄ of 27, 139, and 1026, respectively, greater than 550 °C membranes for 5, 12, and 11. The 750 °C carbon–SiO₂–ZrO₂ membrane maintained strong H₂ permeance and selectivity and was more stable during hydrothermal conditions.

Wang et al. prepared ZrO₂–MSiO₂ membranes to improve SiO₂ membrane steam stability and H₂ perm selectivity.³⁸ The materials' pore size distribution and average pore size increased after ZrO₂ doping, demonstrating that ZrO₂ expanded the pores. ZrO₂–MSiO₂ membranes showed good pore structure and micropore/mesoporous ratio, improving natural gas permeance. These membranes had 79.18% and 26.75% higher H₂/CO₂ and H₂/N₂ selectivity at 200 °C compared to bare SiO₂. In addition, at 0.4 MPa, the perm selectivity remained greater than their Knudsen diffusion, showing excellent gas permeance. Yan et al. studied methyl-modified membranes and their variants doped with nickel and cobalt to improve separation characteristics and hydrothermal stability.³⁶ Pressure, temperature, Ni/Co content, and hydrothermal stability were used to estimate membrane H₂ permeances and permselectivities. Ni–Co/MSiO₂ materials contain Si–O–Ni/Si–O–Co links and NiO/CoO. The Ni_{0.024}Co_{0.056}/MSiO₂ membrane has $7.6 \times 10^7 \text{ mol} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$ H₂ permeance and 113.5 H₂/CO₂ permselectivity at 0.3 MPa pressure difference at 200 °C. H₂ permeance and H₂/CO₂ permselectivity of the Ni_{0.024}Co_{0.056}/MSiO₂ membrane rose to 2.8 times after steam treatment and regeneration, however, the performance of the MSiO₂ membrane fell. Ni–Co/MSiO₂ membranes demonstrated good hydrothermal stability and H₂/CO₂ permselectivity. Because of the poor hydrothermal stability, the silica-based membranes have been barely used over 500 °C such as the conditions for natural gas steam reforming and ethanol steam reforming.³⁹ Guozhao Ji et al. investigated the hydrothermal stability of a silica-cobalt membrane under harsh conditions as high as 20% of steam and 550 °C.⁴⁰ It was noted that employing a cobalt-silica membrane resulted in 4.32 mL min^{−1} of H₂ production continuously with a purity of 82.12 vol % as compared to the case without membrane that gives 2.34 mL min^{−1} of H₂ with a purity of 65.0 vol % without a membrane. The pores size for membranes can be altered by filling with various-sized silica particles to achieve good permeability and selectivity.⁴¹ In addition, other ceramics can be used for modifying silica membranes to enhance membrane stability.

2.1.2. Nickel-Based Membranes. A solid Ni matrix with specified pores forms nickel porous membranes.^{42–44} Pure Ni or Ni alloys are used to make unsupported Ni porous membranes, which are used as a support for a secondary metal selective layer. Furthermore, ceramic and metal-supported Ni membranes have been extensively studied. Different manufacturing methods affect the shape of these membranes (pore depth size, and porosity). The gas transport mechanism depends on pressure, temperature, mean free path, and pore size distribution. Pure nickel porous membranes have tiny and homogeneous pore diameters, making them excellent membrane supports. Multiple Ni alloy membranes have been used in hydrogen purification systems.^{45–47} V, Nb, Ta, and Pd have strong hydrogen diffusivities and solubilities, making them popular in membrane technology. Hydrogen embrittlement occurs in pure V, Nb, Ta, and Pd at temperatures below 573 K

and pressures below 2 MPa.⁴⁸ Ni in bcc structure metals (V, Nb, Ta) and palladium lowers hydrogen embrittlement, improving membrane mechanical stability.^{49–52} Dense Ni-based membranes can be self-supporting or placed on porous supports.⁵³ Thicker foils make unsupported dense Ni membranes that resist hydrogen infiltration. Mechanical stability was improved by depositing thin Ni films on different supports such as Vycor glass,⁵⁴ alumina,^{55,56} and stainless steel.⁴⁷ Ceramic substrates are also being used to support thin Ni films. However, Ni adheres poorly to ceramic supports, thus proper cleaning^{57,58} and treatment⁵⁹ are required before deposition. Al₂O₃ makes a suitable composite of Ni for H₂ separation. Park et al.⁶⁰ synthesized Al₂O₃ membranes using sol–gel and cemented Ni particles using hot press sintering to increase membrane strength and substrate adherence. Support quality determines membrane film thickness. Ni porous supports, with smooth surfaces and homogeneous pore sizes, may be employed without surface modification for various types of supports, however, intermolecular diffusion avoidance continues to be a problem.^{61,62}

Wang et al. looked into Ni hollow fiber membranes.^{63,64} In one of their studies, a dry-wet phase-inversion approach was used to create compact Ni hollow fiber membranes.⁶⁴ The Ni hollow fiber membrane is used to separate pure H₂ from reformed mixes. In reformed gases, Ni membranes have high thermal and chemical stability. Because of the WGS reaction, H₂ recovery is strongly reliant on CO and CO₂ concentrations. The dry-wet spinning and sintering technology was used to create metallic Ni hollow fiber membranes with narrow wall thickness and optimal microstructure. The produced Ni hollow fibers have a high H₂ permeability and 100% H₂-permselectivity, allowing hydrogen penetration only at high temperatures. The WGS reaction that occurs in the presence of CO, CO₂, and H₂O may have a significant impact on hydrogen recovery from reformed mixtures (vapor). At high temperatures, the Ni hollow fiber membranes also exhibit good cycle operating performance and high resistance to CO, CO₂, H₂O, and H₂S poisoning. The excellent thermal and chemical stability, as well as the high permeation performance, endow the Ni hollow fiber membranes with significant potential in advanced applications such as portable hydrogen delivery devices or integration with hydrogen production from coal gasification or methane reformers to improve plant efficiency, which is the most promising and realistic near-term technology for large-scale hydrogen production. Wang et al. also prepared metallic nickel asymmetric hollow fiber membranes with a dense skin on a porous substrate in a single-step synthesis.⁶³ The nickel asymmetric hollow fibers have H₂ fluxes that are 6–8 times higher than the symmetric capillary membranes. Nickel asymmetric hollow fibers can be used directly in methane steam reforming to produce hydrogen. At 1000 °C, the maximal H₂ generation rate of the Ni hollow fibers is 50.84 mmol·s⁻¹. At temperatures above 800 °C, the Ni hollow fiber membranes exhibit great chemical stability and resistance to carbon deposition.

Jiang et al. investigated the microstructures, mechanical characteristics, and hydrogen permeability of V–Ti–Ni alloy membranes with an identical Ni/Ti atom ratio.⁵² According to their findings, V₆₀Ti₂₀Ni₂₀ alloy has better strength and hardness than V₇₀Ti₁₅Ni₁₅ alloy due to a combination of solid solution hardening and particle strengthening. Hydrogen permeability testing reveals that the V₆₀Ti₂₀Ni₂₀ alloy is more resistant to hydrogen embrittlement than the V₇₀Ti₁₅Ni₁₅ alloy,

making it a more suitable material for hydrogen separation applications.

Deng et al. investigated the creation of pure hydrogen via metal membranes, with a particular focus on nickel hollow fiber membranes.⁶⁵ Higher sintering temperatures resulted in denser and thinner nickel hollow fiber membranes, whereas lower temperatures caused higher hydrogen permeability owing to larger grain boundaries. It was reported that the longer sintering times removed organic residue, while shorter time caused flaws. On the contrary, sintering duration had a smaller effect on grain size. They stated that 1100 °C was the best sintering temperature for the maximum hydrogen flux. As a result, lower sintering temperatures, longer sintering periods, and higher hydrogen concentrations are all beneficial in the production of high-performance nickel hollow fiber membranes. The research provides insights into producing cost-effective and productive nickel hollow fiber membranes.

Escalante et al. studied autocatalytically deposited PdNiAu composite membranes with various compositions and thicknesses.⁶⁶ Using the NiPdAu deposition sequence and thermal treatments under an H₂ gas environment, the alloy was formed in a single FCC phase. It was observed that as Ni concentration increased, lattice properties decreased. Film thickness ranged from 8 to 16 μm depending on alloy composition and deposition cycles. They showed that composite membranes acted like a solution-diffusion mechanism, with hydrogen diffusion into the alloy layer limiting phase. Increased Ni content reduced perm selectivity. The 29% At membrane Ni exhibited the best H₂ permeance at 723 K and 100 kPa (11.40 × 10⁻⁴ mol·m⁻²·s⁻¹·Pa^{-0.5}) exceeding the performance of pristine Pd. The stability of prepared membranes was confirmed even after 10 days of period at high temperatures.

There is a modest amount of H₂ purification achieved by using porous membranes, such as ceramics made from aluminum zirconium or silicon oxides.⁶⁷ It is possible to mix porous membranes with other types of cleaning processes. Ceramic membranes have a high level of resistance to gas mixtures containing carbon oxides and sulfur compounds. They can be used as a pretreatment to lengthen the lifespan of cleaning procedures that rely on catalysts and are ideal for this purpose. The usage of porous membranes that have a thin catalytic layer is becoming increasingly common. Ceramic membranes are sensitive to deterioration when water vapor is present in the environment. The disadvantages are also present in carbon membranes. The operation of certain vapors requires extremely high temperatures because of the powerful sorption that they exhibit. They are not only tough to produce but also difficult to run.

2.1.3. Pd-Based Membranes. Membranes made of Pd and its alloys are capable of operating at very high temperatures and pressures and they exhibit the highest permeation rate and selectivity. For instance, the hydrogen purity of 99.99% can be reached with a Pd-based membrane.^{68,69} Pd composite membrane reactor packed with a commercial Ru/Al₂O₃ catalyst was used to produce hydrogen with CO₂ capture under mild operating conditions.²² The fabricated Pd composite on a tubular stainless steel support via the electroless plating method displayed an H₂ permeance of 2.26 × 10⁻³ mol m² s⁻¹ Pa^{-0.5}, H₂/N₂ selectivity of 145 at 773 K, and pressure difference of 20.3 kPa. The use of Pd-membrane has challenges such as high cost and weakness at high temperatures (more specifically greater than 573 K) to

some specific chemicals, such as HCl, CO, CO₂, and H₂S which can result in performance loss. One of the biggest challenges of Pd-based composite membranes is the sulfur poisoning. Therefore, alloying Pd metal with other inexpensive metals such as copper, nickel, silver, and titanium can be a solution to sulfur poisoning by reducing the system cost.⁷⁰ For instance, some recent reports showed that Pd–Au–Ag alloy membranes exhibited several advantages including improvement of resistance against catalytic poisoning and decrease of embrittlement.^{71,72}

2.2. Steam Reforming of Ethanol. At a small scale, a light alcohol steam reforming Pd membrane reactor might integrate a reformer and separator for low energy consumption and high throughput flexibility. Because they selectively remove H₂, Pd membrane reactors are good for steam reforming. During prolonged operation, carbonaceous chemical adsorption reduces its H₂ permeability. Zhao et al. used a simple one-step hydrothermal method and silane coupling treatment to protect the Pd membrane from water and mild alcohol.⁷³ The zeolite layer protected the Pd bulk from harmful species, and silanization increased hydrophobicity on the TS-1/Pd composite membrane by lowering hydroxyl density. The TS-1/Pd membrane had 0.95% carbon content after 100 h of steam reforming, compared to 13.20% for the pure Pd membrane. H₂ permeability and H₂/N₂ selectivity of TS-1/Pd membrane remained steady, but pure Pd membrane decreased by 50% and 80%, respectively. The enhanced carbon deposition resistance of the Pd membrane reactor enables large-scale hydrogen production via steam reforming.

Numerous theoretical studies have estimated the benefits of membrane integration with ethanol steam reforming (ESR).⁷⁴ This research sought to increase catalytic steam reforming and CO removal efficiency to produce high-purity H₂ for PEM fuel cells. Manzolini et al. examined energy efficiency in three reactor configurations: a traditional system with an ethanol reformer, high and low-temperature WGS converters, and a preferential oxidation unit, and a traditional system with an ethanol reformer, WGS with membrane, and CMR for ESR and H₂ purification.⁷⁵ The second and third configurations achieved net electrical efficiencies of 39% and 41%, 7% and 9% higher than the baseline system. Reducing the molar input steam-to-ethanol (S/E) ratio increased efficiency notwithstanding coke danger. Mendes et al. evaluated membrane and conventional reactors for PEM fuel cell H₂ generation.⁷⁶ With an ethanol reformer, high and low-temperature WGS converters, and a selective oxidation reactor, the typical system filtered H₂. WGS and H₂ were removed by membrane reactors. From conventional to membrane reactor streamlined design and increased energy efficiency from 27% to 30% at 773 and sorption-enhanced reactors.⁷⁷ The best H₂ yield and lowest carbon formation were achieved by a hybrid system.

2.3. Reforming and Gasification of Biomass. The generation of hydrogen from waste glycerol, a byproduct of biodiesel synthesis, is being investigated as a renewable energy source for future applications. Saidi et al. employed mass transport phenomena, thermodynamic criteria, and chemical process kinetics to predict glycerol steam reforming using membrane technology.⁷⁸ Sensitivity analysis was performed on operating parameters for glycerol conversion, hydrogen yield, and hydrogen recovery. Glycerol conversion is limited by a high feed molar ratio and sweep ratio while operating pressure and temperature boost it. Sweep gas ratio and temperature increase hydrogen permeation and recovery. This study looked

at glycerol steam reforming in one phase utilizing a Pd–Ag membrane reactor to create and separate hydrogen. The effects of feed molar ratio, reaction temperature, pressure, sweep gas ratio, and sweep gas temperature on glycerol steam reforming performance have been investigated. Because warmth promotes glycerol reformation and hydrogen penetration, hydrogen recovery rises as reaction temperature rises. A high sweep gas ratio and reaction pressure can assist hydrogen penetration and recovery at the expense of lower temperatures. A higher sweep gas temperature minimizes reaction heat loss, resulting in a higher hydrogen yield. Finally, research in membrane technology using a detailed mathematical model based on common industrial operating conditions can enable large-scale hydrogen synthesis from waste glycerol.

Parente et al. explored biogas valorization using dry and steam reforming to produce pure H₂ and/or syngas while reducing net CO₂ emissions.⁷⁹ Multifunctional membrane reactors with hydrogen perm-selective membranes were employed. Comparing the membrane reactor, which produces ultrapure hydrogen in the permeate, to a traditional reactor. Thermal equilibrium simulations using Gibbs free energy minimization were used for all evaluations. The conventional reactor was heated to 800 °C and the membrane reactor to 550 °C. The effect of feedwater on hydrogen and CO₂ reduction productivity was also examined. Because it can operate at high temperatures, the traditional reactor produces syngas with great purity (just CO and H₂). Based on water cofed, the syngas H₂/CO ratio can be modified for other purposes. The permeate side of the membrane reactor produces high-purity hydrogen at 73 mol per 100 mol of biogas input. Assuming the biogas generation capability of a current landfill site, this productivity produces 131 kg/h of H₂. CO₂ recycling can cut net CO₂ emissions by 50%. We found that dry and steam reforming with low water content in the feed of a hydrogen-selective membrane reactor increases methane conversion (or at a lower temperature than in a typical reactor) and pure hydrogen production in the permeate.

Osat et al. modeled gas and solid nonisothermal zones in conventional and membrane fluidized-bed trireformers for the first time.⁸⁰ The traditional trireformer was validated with experimental data and enhanced to the membrane fluidized-bed trireformer. First, a systematic analysis examined how operating variables affected reaction rates. Results show that a large volume fraction of dispersed phase and hot zone development cause high reaction rates when raw materials are fed into the reactor. Thus, species production and consumption increase near the reactor inlet. A single-objective optimization was then performed to maximize H₂ generation in the traditional fluidized-bed reactor. At an inlet temperature of 804 °C, flow rate of 3.6 × 10⁵ L h⁻¹, and H₂O/CH₄ ratio of 2.5, the traditional fluidized-bed reactor yields maximal H₂ (1.37). Finally, a membrane-assisted reactor was modeled under the optimized conventional fluidized-bed reactor operating conditions. At low temperatures, the hydrogen perm-selective membrane reactor converts less CH₄ than the fluidized-bed trireformer. CH₄ conversion in the hydrogen perm-selective membrane reactor surpasses that of the fluidized-bed trireformer at roughly 800 °C input temperature. The WGS reaction reduces CO₂ conversion in the hydrogen perm-selective membrane reactor compared to the fluidized-bed trireformer. Compared to the cocurrent and fluidized-bed trireformer, the countercurrent hydrogen perm-selective membrane reactor increases H₂ yield by 0.3 and 0.65,

Table 1. Literature Reports Are Based on Composite Membranes for H₂ Generation via the Reforming Process

material	temperature (K)	selectivity	permeance (mol·m ⁻² s ⁻¹ Pa ⁻¹)	ref.
SiO ₂ -Al ₂ O ₃	1073	203	9.0 × 10 ⁻⁷	31
SiO ₂ ZrO ₂	873	1600	2.1 × 10 ⁻⁵	32
carbon-SiO ₂ -ZrO ₂	850	1026	2.8 × 10 ⁻⁷	33
carbon-SiO ₂ -ZrO ₂	473	148	16 × 10 ⁻⁷	34
carbon-SiO ₂ -ZrO ₃	383	573	3.9 × 10 ⁻⁹	35
Ni-Co/SiO ₂	473	113.5	7.6 × 10 ⁻⁷	36
methyl-modified ZrO ₂ -SiO ₂	473		6.46 × 10 ⁻⁶	38
Ni-Ta/Ni	773		7.8 × 10 ⁻¹¹	50
V-Ti-Ni	673		4.2 × 10 ⁻⁸	52
Pd-based/PSS	773	145	2.26 × 10 ⁻³	22
Pd-based/PSS	673	9000	3.79 × 10 ⁻³	82
Pd/Al ₂ O ₃	673	>4000	3.27 × 10 ⁻⁶	83
Pd/NiO/YSZ/NiO/PSS	773	~87	3.81 × 10 ⁻³	84

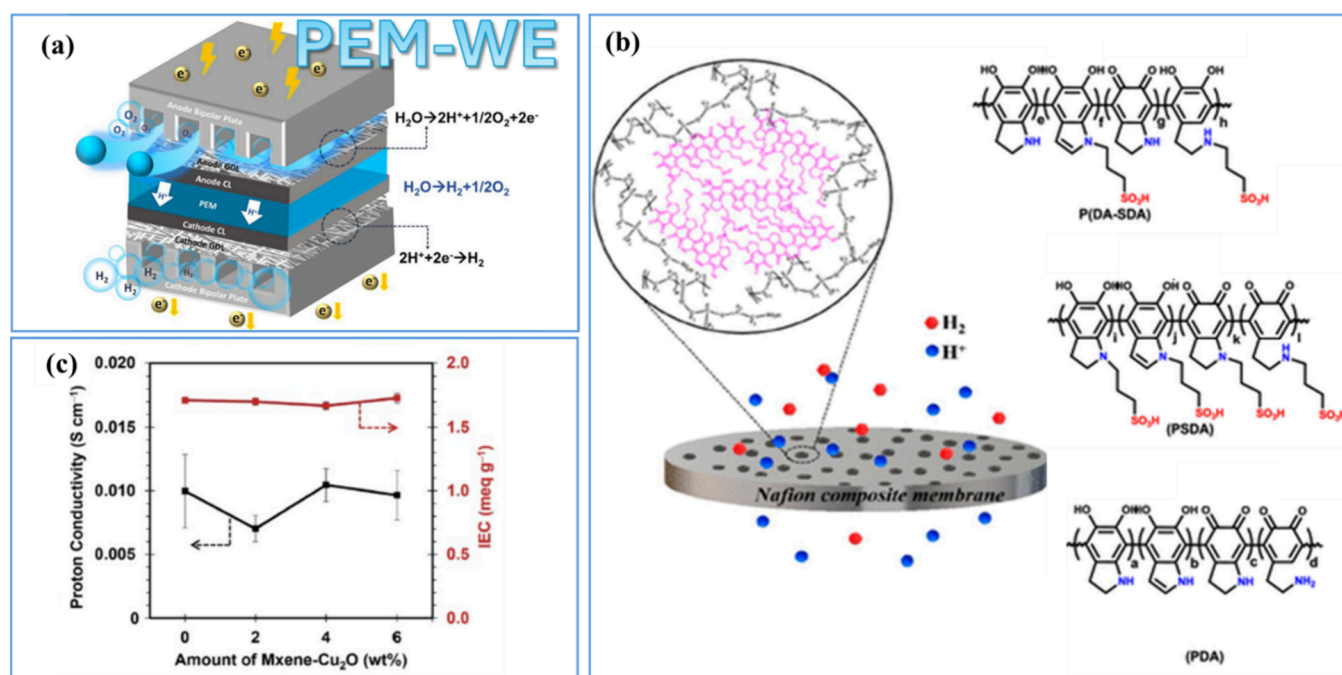


Figure 2. Schematic illustration of (a) a PEM electrolyzer (Reprinted with permission from ref 87 Copyright 2023 IOP Science), (b) composites of polydopamine and Nafion-212 membranes (reproduced with permission from ref 90, Copyright 2022 American Chemical Society), (c) comparative ion exchange capacity (IEC) and proton conductivity values between SPEEK and composite membranes depending on weight percentages of MXene-Cu₂O additives (reprinted with permission from ref 88, Copyright 2023 Elsevier B.V.).

respectively. The H₂ recovery research shows that raising the retentate side operating pressure and sweep gas velocity increases H₂ recovery. Finally, switching from a cocurrent to a countercurrent hydrogen perm-selective membrane reactor greatly improves H₂ recovery. H₂ recovery is optimal at 20 bar retentate pressure and 3.6 × 10⁵ L h⁻¹ permeate inlet flow rate.

Iulianelli et al. investigated steam reforming over Pd-based membrane reactors of a biogas mixture including hydrogen sulfide (H₂S). Pd-Au/Al₂O₃ and commercial Pd-Ag membranes were both tested.⁸¹ Despite being extremely permeable to hydrogen, the Pd-Au/Al₂O₃ membrane demonstrated lower methane conversion and hydrogen recovery in the presence of H₂S. The Pd-Ag membrane performed better in terms of conversion at lower temperatures but declined faster due to the unfavorable influence of H₂S, resulting in irreversible failure. The study reveals that the Pd-Au alloy is more resistant to H₂S, although membrane flaws reduce hydrogen perm-selectivity. The hydrogen permeability charac-

teristics of the Pd-Au/Al₂O₃ membrane were restored by feeding pure H₂, allowing it to be reused in further trials. Table 1 lists the literature reports based on composite membranes for H₂ generation via the reforming process.

3. COMPOSITE MEMBRANES FOR RENEWABLE H₂ PRODUCTION

Renewable H₂, so-called green H₂, is still a developing fuel to be replaced with fossil-based hydrogen in many applications such as transportation and renewable power units' fuel. Thus, the concern of H₂ production has shifted to renewable processes such as electrolysis from classical natural gas reforming. In a standard electrolysis process, an electrolyzer utilizes electricity to split water molecules into its constituent elements H₂ and O₂. However, the high cost of electrolysis urges the energy field to search for more economical alternative processes.⁸⁵ The produced H₂ is a renewable fuel if the electricity is obtained from renewable power sources

such as wind or photovoltaics directed from solar energy. Solar energy can be used directly to generate H₂ by photoelectrochemical or photocatalytic processes as well. This section focuses on the H₂ generation from renewables linked to composite membranes.

3.1. Composite Membranes for Electrolyzers. Water electrolysis is regarded as one of the most environmentally friendly strategies for H₂ generation because this technology generates H₂ gas without any CO₂ emission. Commercialized water electrolysis currently relies on two types of electrolyzers: Alkaline Water (AW) and Polymer Exchange Membrane (PEM) electrolyzers. Among water electrolysis, PEM-based water electrolyzers that employ proton exchange membrane (PEM) are widely studied types as they generate high efficiency while eliminating risks of electrolyte leakage. However, the use of precious metal catalysts (Pt and IrO₂) increases the cost of the systems. AW electrolyzer, on the other hand, is widely used for commercial applications because the cost-effective catalysts (Fe, Co, Ni) can be employed instead of noble catalysts. The featured literature reports on the use of composite membranes in water electrolysis systems are presented in this section.

3.1.1. Proton Exchange Membrane (PEM) Electrolyzers. A PEM electrolyzer is composed of an anode, cathode catalysts, and a dense acidic PEM in the form of a solid electrolyte (e.g., Nafion, Dupont). PEMs are a highly influential component in both PEM fuel cells and PEM water electrolyzers since they directly affect the overall performance of the membrane by conducting H⁺ ions from the anode to the cathode and separating hydrogen and oxygen gases formed during the reaction (Figure 2a).^{6,86,87} Because of the low gas crossover rate of polymer electrolytes, the PEM electrolyzer can operate at a current density of 2 A cm⁻² by producing higher purity of the gases as compared to AWE systems. However, an acidic environment results in some limitations when choosing materials. Thus, a great deal of studies have been performed on the development of PEM materials with enhanced ionic conductivity and stability.⁸⁸ The superior proton conductivity, excellent chemical stability, and durability established perfluorosulfonic acid (PFSA)-based membranes, more specifically, Nafion as state-of-the-art PEM. Nafion consisting of a perfluoroalkyl-based main chain and side chains of sulfonic acid groups is the most used commercial PEM material owing to its high ionic conductivity, exceptional mechanical properties, and electrochemical stability.⁸⁹ However, the numerous shortcomings such as high cost, significant gas crossover, and the debility for fluorine contamination cannot be ignored. Besides, the mechanical properties of Nafion can be affected at high temperatures and under high humid conditions due to the decrease in glass-transition temperature (*T_g*). Therefore, the preparation and characterizations of the composites of Nafion membrane and various inorganic materials have been under consideration by various research groups for PEM H₂ production. The composite membranes have been expected to have enhanced thermal and mechanical stabilities in an acidic environment. The biggest challenge in front of the composite membranes to be commercialized is the lower proton conductivity and durability as compared to commercialized Nafion membrane. Therefore, extensively research has been performed to obtain PEM with enhanced properties.

For instance, polydopamine and Nafion-212 membranes were used to prepare composite membranes of poly(sulfonated dopamine), and poly(dopamine-co-sulfonated dopamine) via

the swelling–filling method (Figure 2b).⁹⁰ It has been reported that the process resulted in improved thermal and mechanical stabilities due to the compelling interactions between polydopamine derivatives and the Nafion matrix. Thus, the hydrogen permeability of the composite membrane was reported as 27.3% lower in a fully hydrated state (water electrolysis operating conditions) than Nafion-212. A nanocomposite membrane based on an electrospun polysulfone fiber web and short-side-chain Aquivion perfluorosulfonic acid was synthesized by the impregnation process to be used in the application of the PEM water electrolysis system by Stefano Giancola et al.⁹¹ This work reported that the nanofibre web reinforcement enhanced the mechanical and dimensional stability while reducing hydrogen crossover.

The use of inorganic additives in polymer membranes was reported by Antonucci et al.⁹² The research group prepared a composite Nafion-SiO₂ type membrane for PEM electrolysis operating at 120 °C. The composite membrane performed better as compared to Nafion 115 having a similar thickness. In recent research, the inorganic additives in a polymeric membrane were investigated in PEM water electrolysis applications. A composite MXene-Cu₂O/SPEEK membrane was prepared and explored in terms of proton transfer in a WE process.⁹³ The synthesized composite membrane having a 4% MXene-Cu₂O/SPEEK configuration showed the best proton conductivity of 0.0105 S cm⁻¹ at 30 °C (Figure 2c). In another work, a composite of Nafion with the lanthanides Cerium and Zirconium was compared with pristine Nafion and it was reported to enhance the proton conductivity by 17% with loading of 3 wt % Ce-UiO-66 (124.45 mS/cm).⁹⁴ The compositing of monolayer hexagonal boron nitride (hBN) with Nafion 117 has been investigated for the PEM water electrolyzer.⁹⁵ Introducing monolayer hBN, the mechanical strength increased as H₂ permeability significantly diminished as compared to that of pristine Nafion (~40%). Graphene-modified commercial Fumapem membranes containing different graphene loadings for PEM water electrolysis application resulted in enhancement in the proton conductivity.⁹⁶ In research work, tungstophosphoric acid (TPA) with cesium (Cs) was used as additives to the sulfonated polyether ether ketone (SPEEK) to increase proton conductivity, while CeO₂ was to improve the durability of the membrane in the preparation of a covalently cross-linked SPEEK/Cs-TPA/CeO₂ composite for the polymer electrolyte membrane water electrolysis.⁹⁷ The H₂ flow rate of gas evolution was observed faster (3.68 mL min⁻¹) than that of a pristine SPEEK membrane when using the mentioned composite as an H⁺ ion exchange separator in the water electrolysis system.

Incorporation of a gas recombination catalyst (GRC) layer such as Pt or its alloys (Pt/Co) layer into commercially available membranes to avoid hydrogen crossover and results in a more efficient and robust electrolysis system for hydrogen production.^{98,99} For instance, the cell voltage for the recombination catalyst incorporated MEA prepared from the perfluoro sulfonic acid membrane was approximately 30 mV lower than the pristine MEA during the stability measurements.⁹⁹ The GRC incorporated MEA exhibited low-performance losses during 3500 h at 4 A cm⁻². In the same way, electroless Pt layer deposition on various types of Nafion membranes was proposed to obtain MEA with diminished hydrogen crossover and ohmic resistance for PEM water electrolysis.¹⁰⁰

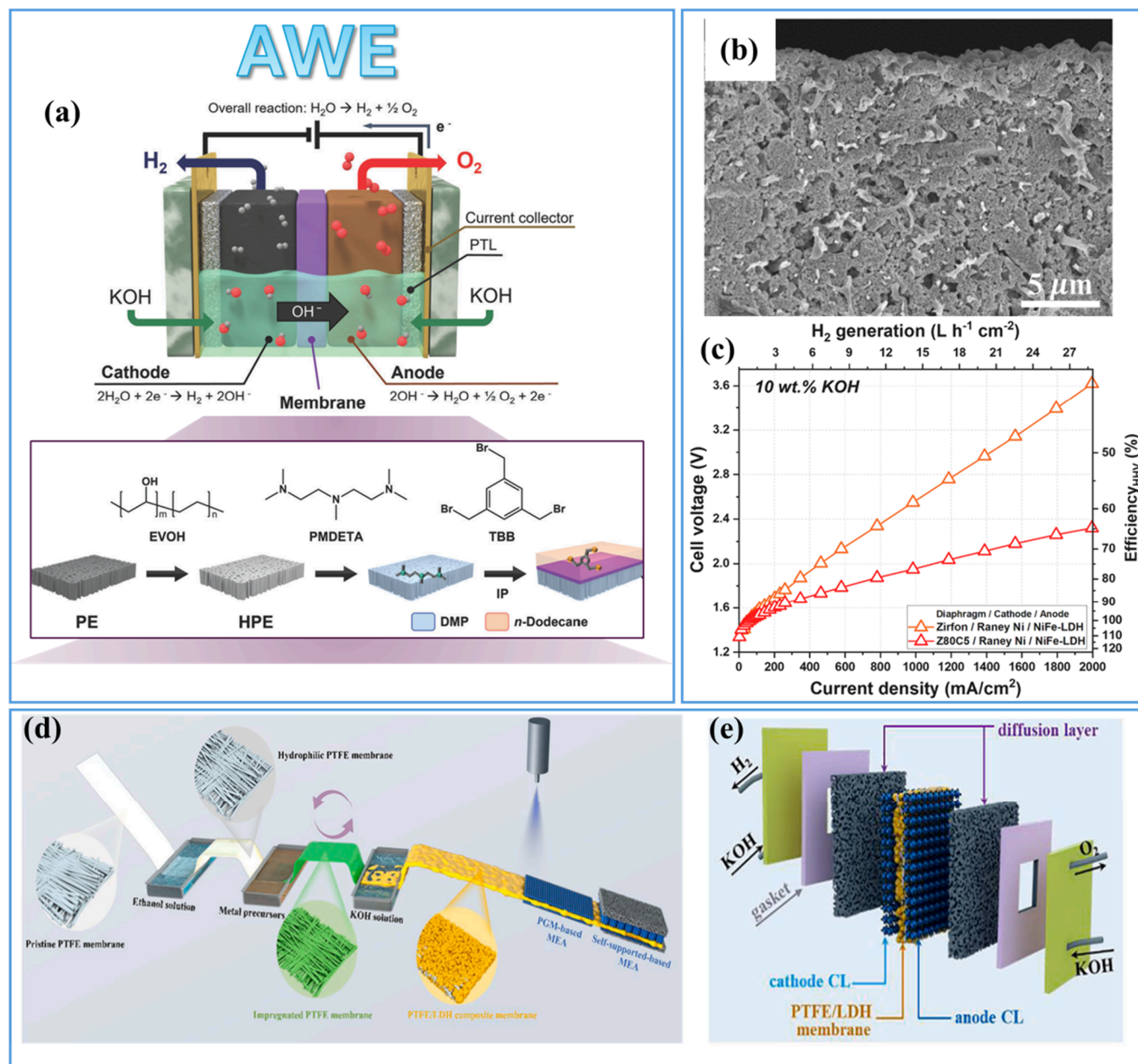


Figure 3. (a) Schematic representation for an AWE cell and composite membrane production steps (reproduced with permission from ref 103, Copyright 2024 John Wiley and Sons.), Zirconia/Polysulfone composite membrane with cellulose nanocrystals; (reprinted with permission from ref 101, Copyright 2021 Elsevier B.V.), (b) cross-sectional SEM image, (c) cell performance of alkaline cells with 10 wt % KOH, (d) the preparation process of MEA based on PTFE/LDH composite membranes by pore-filling method, (e) and schematic illustration of the designed AWE (reprinted with permission from ref 104, Copyright 2021 Elsevier B.V.).

3.1.2. Alkaline Water Electrolysis (AWE). The AWE employing composite membranes is reported to improve the physical properties of the membrane separator and thus, to ensure performance enhancement.^{101–104} In this context, Choi et al. prepared a thin film composite membrane for AWE systems.¹⁰³ The proposed membrane was prepared by the formation of an ultrathin quaternary ammonium selective layer on a porous polyethylene support (Figure 3a). The favorably anion-conductive quaternary ammonium layer supported the prevention of gas crossover and the resulting alkaline-stable membrane resulted in an AWE performance of 1.16 Acm^{-2} (@1.8 V, 80 °C) using nonprecious group metal electrodes with an aqueous solution of KOH (25 wt %).

To prepare a hydroxide ion conduction membrane with highly alkaline resistance for advanced AWE, a large-scale and green preparation strategy that membrane is proposed to fabricate robust alkaline composite membranes, and simultaneously enhance the interfacial compatibility between the catalyst layer and membrane in membrane electrode assembly (MEA) (Figure 3b–e).¹⁰⁴ Upon the rational design, the PTFE/layered double hydroxide (LDH) composite membranes exhibit good hydroxide conductivity, excellent wettability, and exceptional alkaline stability, especially showing no change of the area resistance during 2000 h test in 1 M KOH solution at 60 °C. In advanced AWE, the MEA with PTFE/LDH composite membranes and precious group metal-free (PGM-free) catalysts specifically showed a voltage of 1.8 V at

the current density of 1 A cm^{-2} , while that of commercial Fumasep FAA-3-50 membrane was 2.15 V . The long-term stability is conducted at a current density of 500 mA cm^{-2} for 180 h. Such performance with low-cost and mass-produced PTFE/LDH composite membranes demonstrates that the large-scale and green preparation strategy may drive the development of membranes for renewable hydrogen generation.

Yuan et al. reported the preparation of composite membranes based on alkanolamine-modified zirconia (ZrO_2) particles by a one-pot method for alkaline water electrolysis.¹⁰² Diethanolamine (DEA)-functionalized ZrO_2 separator was reported to display high electrochemical performance with a current density of 1114 mA cm^{-2} at 2.0 V with Raney Ni as the cathode catalyst and CoMnO@CoFe layered double hydroxide (LDH) as the anode catalyst at $80 \text{ }^\circ\text{C}$ along with high stability for over 150 h. Recently, a composite membrane consisting of polysulfone (PSU), zirconium dioxide (ZrO_2) nanoparticles, and polypropylene (PP) nonwoven fabric utilized an AW electrolysis system with a current density of 2.3 A cm^{-2} at 2 V ($30 \text{ wt } \% \text{ KOH}$, $80 \text{ }^\circ\text{C}$) has been reported.¹⁰⁵ In this work, Y. Liao et al. emphasized that they produce hydrogen gas with a purity of $\sim 99.997\%$, which is higher than that of the commercial ZIRFON UTP 500 membrane. Composite membranes utilizing AW electrolysis show a great diversity in terms of the inorganic part as well as the type of polymeric matrix. As stated in the review articles that summarize many successful studies on this subject, each membrane system has its advantages and disadvantages.^{106–109} The study based on composite membrane described a preparation method using grafting and cross-linking of base-catalyzed *N*-methyl-4-piperidone-formaldehyde-based prepolymer on poly(vinyl alcohol) using additives tetraethyl orthosilicate (TEOS) and zirconium oxychloride. The water-splitting performance of this proposed composite membrane electrode assembly was compared with commercially available Neosepta membranes.¹¹⁰ Studies in this field show that composite membranes with high performance, long life, and cost-effective production will continue to be studied without losing their importance in the future to investigate the use of green hydrogen production.

To prepare a hydroxide ion conduction membrane with highly alkaline resistance for advanced AW electrolysis, a large-scale and green preparation strategy that pore-filling polytetrafluoroethylene (PTFE) membrane is proposed to fabricate robust alkaline composite membranes, simultaneously enhance the interfacial compatibility between catalyst layer and membrane in membrane electrode assembly (MEA).¹⁰⁴ Upon the rational design, the PTFE/layered double hydroxide (LDH) composite membranes exhibit good hydroxide conductivity, excellent wettability, and exceptional alkaline stability, especially showing no change of the area resistance during 2000 h test in 1 M KOH solution at $60 \text{ }^\circ\text{C}$. In advanced alkaline water electrolysis, the MEA with PTFE/LDH composite membranes and precious group metal-free (PGM-free) catalysts specifically showed a voltage of 1.8 V at the current density of 1 A cm^{-2} , while that of commercial Fumasep FAA-3–50 membrane was 2.15 V . The long-term stability is conducted at a current density of 500 mA cm^{-2} for 180 h. Such performance with low-cost and mass-produced PTFE/LDH composite membranes demonstrates that the large-scale and green preparation strategy may drive the development of membranes for advanced AW electrolysis.

S.S. Kumar et al. reported the titanium(IV) oxide composite membrane for AWE.¹¹¹ In their studies, it was aimed to use the advantages of inorganic/organic composite membranes such as high chemical and thermal resistance, long life, and homogeneous pore distribution. Besides titanium dioxide (TiO_2)-based membranes offer electrical conductivity and high electrocatalytic activity. In this regard, it has been reported that the cell using membranes prepared by $15 \text{ wt } \% \text{ TiO}_2$ powder, poly sulfone, and polyvinylpyrrolidone polymeric structures can produce hydrogen with 99.9% purity at a rate of 30 mL/min when operated at 2 V at $80 \text{ }^\circ\text{C}$ and 30% KOH by weight. It can be concluded that TiO_2 composite membranes can be produced without using any hazardous materials and their cost-effective nature creates a significant potential in AW electrolysis as an alternative to commercial asbestos.

In another study, cobalt-doped nickel/iron layered double hydroxide (Co:NiFe-LDH) nanosheets and poly(vinyl alcohol) (PVA) composite membranes were reported for alkaline water splitting.¹⁸ Transition-metal-based alloys including cobalt, nickel, and iron, have been used as high-performance catalysts for hydrogen evolution reactions (HER).^{112,113} It has been reported that the high d-state electronic center of the transition metal sites and the accessible orbital hybridization between metal and H_{ads} 1 s can benefit from reducing the reaction energy barrier during the HER process.¹¹⁴ The Co:NeFe-LDH@PVA composite membranes, reported by C. Lai et al., exhibited high stretchability and mechanical strength, strong hydrophilicity, and good ionic conductivity.¹⁸ They reported a cell voltage of 1.419 V at the current density of 10 mA cm^{-2} with stability for 100 h.

Although the AWE is deep-rooted in industrial applications, it is currently not suitable for the incorporation of solar energy. In industrial AWE systems, the separator is composed of a porous diaphragm which has the ohmic resistance issue due to the large thickness and thus, restrains the process to low current densities. PEM-WE, on the other hand, employs a thin membrane based on perfluoro sulfonic acid which can enable the process at high current densities in widespread industrial applications. However, in that condition, the use of acidic electrolytes that require the use of noble metals increases the total cost of the operation. An anion exchange membrane (AEM) used in an alkaline solid electrolyte can be a good alternative. However, there is no commercial membrane that meets the requirements of alkaline membrane WE.¹¹⁵ The mechanical stability of AEM can be reinforced by using porous support. For instance, commercial Sustainion membranes were compared with PTFE reinforcement to clear the effects on the device's performance.¹¹⁶ In another study, pore-filling polybenzimidazole nanofiber mats with the Bromo methylated precursor of mTPN have been proposed to achieve a stable AEM material.¹¹⁷

3.2. The Hybrid Sulfur Cycle. This process has drawn attention in recent years as being a more economical alternative to electrolysis.^{118,119} It is under serious consideration internationally for hydrogen production in large quantities. Additionally, this process can be integrated either with a concentrating solar source or a nuclear source to generate green hydrogen. Same as the other types of electrolysis systems, in this process water molecules are split into H_2 and O_2 gases through the recirculation of sulfur compounds. Nafion membranes which operate at temperatures lower than $80 \text{ }^\circ\text{C}$ are commonly studied membranes for the

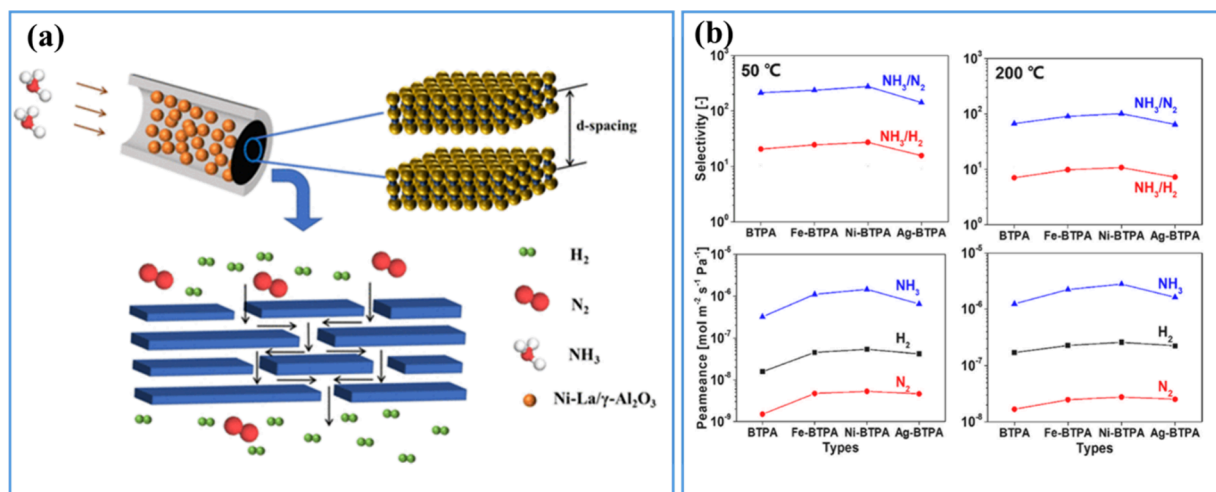


Figure 4. (a) Schematically illustrated NH₃ decomposition and H₂ permeation in the MXene-based composite membrane reactor (reprinted with permission from ref 135, Copyright 2023 American Chemical Society), (b) NH₃ permeance and selectivity at 50 (left) and 200 °C (right) as a function of metal affinity of bare and metal-doped BTPA membranes prepared by W.-W. Yan et al. (reprinted with permission from ref 139, Copyright 2023 Elsevier B.V.)

process.^{120,121} However, the latest research shows that the electrolysis above 100 °C is more profound for better water management and higher overall thermal efficiency of the hybrid sulfur cycle.^{122,123} In this condition, the Nafion membranes which have an operational limitation below 80 °C must be replaced with more resistant membranes.

Polybenzimidazole membranes, in this case, are good alternatives as they can operate at higher temperatures and are chemically stable in acidic and alkaline electrolytes.^{119,124,125} Inorganic composite fillers to prepare composite membranes have been proven to increase the performance of the membrane for hydrogen production in the process. For instance, TiO₂ has been proposed as an inorganic composite filler for this type of membrane and resulted in an enhancement in hydrogen production rate.¹¹⁹ Another inorganic filler is graphene oxide (GO) in polybenzimidazole membranes has been proven to be a good alternative to enhance performance.^{126,127} In the study reported by Sergio Diaz-Abad et al. PBI membranes with GO contents in various weight ratios (0.5, 1.0, 2.0, and 3.0 wt %) as inorganic additives were investigated in SO₂-depolarized electrolysis for hydrogen production, and 2.0 wt % of GO addition resulted in the highest H₂ evolution as 2.2 mLmin⁻¹A⁻¹.¹²⁷

3.3. Ammonia Decomposition Process. Ammonia (NH₃) is considered an energy carrier with a high hydrogen storage capacity (17.7 wt %) and it can be easily liquefied at mild conditions (20 °C and 8.6 bar).^{128–130} The synthesis of ammonia from elemental hydrogen and nitrogen molecules can occur in the presence of precious metal catalysts such as palladium (Pd) and its alloys with Ag, Cu, Ni, and Pt metals. Since performing the catalytic decomposition and the purification of H₂ gas separately is more energy-consuming and complicated, a high yield and purity of H₂ production can be achieved with a compact membrane reactor design.^{131–133} In recent studies, high-purity H₂ production in catalytic membrane reactors employing various catalysts and composite membranes has been reported. H₂-selective membranes developed for NH₃ decomposition are mostly MFI zeolite-, carbon molecular sieve- and Pd–Ag-based membranes.^{128,134,135} Recently, the synthesis of MXene (Ti₃C₂T_x) nanosheets depositing on anodic aluminum oxide was reported

to be used in an NH₃ decomposition reactor attaining an H₂ permeance of 2.85×10^{-7} mol m⁻² s⁻¹ Pa⁻¹ with a selectivity of H₂/N₂ as high as 20 (Figure 4a).¹³⁵

A study based on the inorganic composite membrane for H₂ production from NH₃ decomposition was reported by Tae-Woo Kim et al. preparing a highly selective Pd composite membrane to design a membrane reactor combined with a Ru/Al₂O₃ catalyst, from a tubular porous Inconel 600 support coated with Pd using a vacuum-assisted, two-step electroless plating.¹³⁶ It was reported that the H₂ selectivity increased with Pd electroplating resulting in hydrogen permeation flux and selectivity (H₂/N₂) were 3.40×10^{-1} mol m⁻² s⁻¹ and 8,050, respectively (measured at 723 K and a transmembrane pressure difference of 100 kPa). Additionally, an H₂ recovery ratio of 87% and an H₂ production rate of 0.25 N m³ h⁻¹ with 99.99% purity was reported. The membrane reactor composed of a dense metallic Pd/Ta composite membrane and Ru/La–Al₂O₃ pellet catalyst was reported to achieve ammonia conversion of 99.5% at 450 °C under 6.5 bar pressurized ammonia feed.¹³⁷ In another study, Jose L. Cerrillo et al. reported high-purity H₂ (>99.97% H₂) production from NH₃ decomposition using a composite membrane.¹³⁸

NH₃/H₂ selectivity of the synthesized temperature bis[3-(trimethoxysilyl)propyl] amine (BTPA) membranes with metal (Fe, Ni, and Ag) doping was investigated at various operating temperatures.¹³⁹ The high permeability was directed to the enhanced interaction between Ni-BTPA with NH₃ via metal-induced coordination and hydrogen bonds and/or van der Waals. The results obtained at 200 °C showed that the Ni-doped BTPA membrane exhibited the highest NH₃ permeance of $\sim 2.8 \times 10^{-6}$ mol m⁻² s⁻¹ Pa⁻¹ with ideal NH₃/H₂ and NH₃/N₂ selectivity of 11 and 102, respectively. The NH₃ absorption–desorption amounts of metal doped-BTPA compared with some PFSA polymers such as Nafion and Aquivion at 150 °C along with NH₃ permeance and selectivity at 50 and 200 °C are demonstrated in Figure 4b.

3.4. Composite Membranes for Solar Hydrogen Production. The utilization of water resources and solar energy as the most abundant energy source to accomplish green hydrogen production through solar water splitting has garnered a rising interest for the last three decades.^{140–149}

Inspired by natural photosynthesis, the photocatalytic water-splitting process harvests solar radiation to separate electrons from water molecules and store them in high-energy chemical bonds.¹⁵⁰ Even though the process has great potential for large-scale hydrogen production, the limited suitable catalysts and systems restrict the overall solar-to-hydrogen (STH) efficiency with high efficiency. Photoelectrochemical (PEC) water splitting is a similar process that requires a voltage of 1.23 V. In this section, the composite membranes reported in solar H₂ generation systems are reviewed.

The spatial separation of H⁺ and OH⁻ ions is one of the main problems of photocatalytic/PEC water splitting. Due to the very close radii differences of these ions (2.82 Å for H₃O⁺ and 3.00 Å for OH⁻, respectively), the ionic separation by using porous membranes is still a challenge.¹⁵¹ Perfluorinated polymers such as Nafion are used as proton-conducting polymer electrolyte membranes.¹⁵² However, the high production price and requirement of toxic chemicals in the preparation process is an economical drawback as well as proton conductivity issues at higher temperatures. Therefore, developing composite membranes can improve these drawbacks. However, there is limited work on photocatalytic H₂ generation using composite membranes. Most of the studies rely on the photoelectrochemical/photocatalytic performance of synthesized composite membranes with semiconductor nanoparticles. The membrane electrode performs as a conductive polymer layer to urge the reaction equilibrium for more favored H₂ production while simultaneously transferring H₂.¹⁵³

A two-compartment cell separated with a proton-conducting polymer membrane based on the composite membrane for photocatalytic H₂ generation under sunlight without any electrical or chemical bias was reported by Marschall et al.¹⁵⁴ This composite polymer membrane that acted as both compartment separator and support for coated electrodes and photocatalyst was prepared using sulfonated polyether sulfone and sulfonated mesoporous Si-MCM-41 nanoparticles. In another work, a photoanode made of ZnO/Cu₂S-loaded PVDF polymer membrane was used for solar water splitting application.¹⁵⁵ The PVDF/Ag/ZnO/Cu₂S photoanode was reported to generate a photocurrent density of 0.62 mAcm⁻² in the -0.2 to 0.4 V vs Ag/AgCl potential window. Qianyu Wang et al. reported the utilization of poly(L-lactide) (PLA)/TiO₂/Pt composite fiber membrane in a photocatalytic hydrogen generator.¹⁵⁶ The efficiency of H₂ generation using functional TiO₂ particles loaded on the composite was observed as 30 times higher than that of TiO₂ particles in the aqueous solution. This enhancement led to a 1.8 times increase in the hydrogen generation capability.

In a recent study performed by Weiming Zhou et al., an inorganic composite membrane constructed by a 2D lamellar membrane based on the semiconductor BiOCl nanosheets was studied for photocatalytic H₂ generation.¹⁵⁷ A composite prepared from BiOCl and cellulose nanofibers (CNFs), carbon nanotubes (CNTs), and photocatalytic H₂ generation rates were reported as 25.42 μmol·g⁻¹·h⁻¹ for BiOCl-CNF@CNT nanocomposite lamellar membrane (Figure 5a). In another work, ZnSe, carbon membrane, and TiO₂ nanotube arrays were constructed to get the carbon membrane bridged ZnSe and TiO₂ composite (Figure 5b).¹⁵⁸ Here, the carbon membrane was utilized as electron electron-transferring layer to facilitate charge separation. Consequently, it was reported to reach the H₂ evolution rate of 866.76 μmol·cm⁻² which was

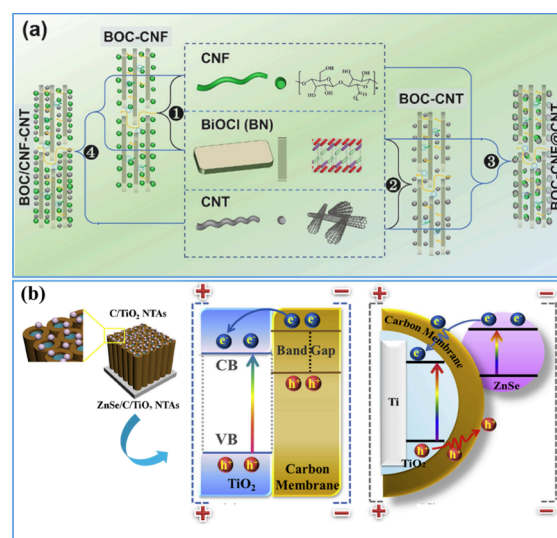


Figure 5. (a) Schematic of the preparation of samples with different composites (reprinted with permission from ref 157, Copyright 2023 Elsevier B.V.), (b) schematic diagram of the charge carrier transfer of ZnSe/C/TiO₂ NTAs under light irradiation (reprinted with permission from ref 158, Copyright 2020 Elsevier B.V.).

~6.95 times higher than that of pristine TiO₂ (124.64 μmol·cm⁻²) after 200 min irradiation.

Photocatalytic ammonia decomposition is another photocatalytic route for H₂ generation which is another emergent process. A composite membrane prepared by intercalation of TiO₂ nanowires with rGO was placed in aqueous ammonia solution and exposed to 254 nm of UV light with 8 W of power intensity for ammonia decomposition.¹⁵⁹ The synthetic photocatalytic membrane was reported to act as a photocatalyst and exhibit H₂ generation at a rate of 208 μmol h⁻¹ g⁻¹ under UV irradiation, which is far more than both TiO₂(P25) and TiO₂ nanowires.

4. CONCLUSIONS AND FUTURE PERSPECTIVES

Hydrogen (H₂) as an energy carrier is of paramount importance in the energy sector and thus, there is a huge requirement for H₂ gas production on a global scale. However, manufacturing at a high yield of H₂ is still an issue. Therefore, developing H₂ gas production techniques in a safe and economical manner is under serious consideration. Besides, increasing the production yield and purity of the H₂ requires a continuous effort. The commonly used in the global H₂ manufacturing systems and featured ones are summarized in this review. The most dominant H₂ production method is still the steam reforming of carbon-based materials. However, this method releases CO₂ emissions and contradicts the global zero emission goal. Water electrolysis, however, is an alternative route for clean H₂ production avoiding the use of carbon-based materials as reactants. It is crucial to reduce production costs as the systems require electricity. Green H₂ can be produced from renewables such as wind and solar power when the electricity can be obtained from these renewables. However, the efficiency is required to be increased for commercial applications. Although all H₂ production methods have pros and cons, the main goal is the develop an economical system to generate H₂ gas for widespread use. Energy technology has focused on enhancing the system's efficiency by improving each component of the system.

Membrane technologies play a critical role in all these H₂ production methods. Currently, the costly Nafion membrane is predominantly used membrane in H₂ generation systems. However, there are issues such as restricting operating temperatures, ion crossovers, and high fuel permeability along with high costs. High-rate H₂ generation strongly depends on the membrane's characteristics such as high mechanical and thermal stability, good electrical insulation and oxidative/hydrolytic stability, low tolerance to ion crossover/good barrier property, and low swelling stress. Many synthetic routes have been applied to enhance these properties of the membranes. Preparing composite membranes via polymer blending, inorganic filler additives, acid or base doping and pores filling are some featured methods to obtain composite membranes for H₂ generation systems. In addition to polymeric membranes, inorganic membranes are also widely used especially for the systems such as photocatalytic H₂ generations and membrane reactors for ammonia decompositions. Therefore, this review focused on the summary of recent developments with composite membranes used in various H₂ production methods, especially to produce green H₂ which is one of the most featured energy applications for carbon-free fuel utilization.

The composite membranes that are employed in the H₂ production methods vary depending on the applications. The reforming of natural gas and methane employs silica, zirconia, and metallic alloy membranes composed of mainly nickel and palladium metals which can produce high purity of H₂. However, there are still some drawbacks to overcome for these types of composite membranes such as liability to sulfur poisoning and embrittlement that should be under consideration. Therefore, much research focuses on developing many types of metal alloy composite membranes to solve this problem. Alternative to Pd-based membranes, silica as a microporous material has become a promising membrane due to its antitoxicity, low-cost, high permeability, high selectivity, and resistance to CO poisoning. However, the major issue of silica membranes is their densification under hydrothermal conditions during H₂ production. The hydrothermal stability of silica membranes can be improved by doping with transition metals or metal oxides. H₂ production through electrolytes without any greenhouse gas emission is certainly the most promising way to achieve green H₂. Therefore, in the past decade, membrane-based electrolysis for hydrogen production has become a growing research interest. Nonetheless, there are still key obstacles to be solved for membrane-based electrolysis can be considered economically viable for large-scale production. The main problems are the high cost, availability, and durability of the membrane. The research on the development of composite membranes focused on producing low-cost and more stable composite polymer membranes by incorporating organic–organic and organic–inorganic additives. Restrictions of these membranes are the limited operational temperature range, low selectivity, low flux, and low tolerance to chemicals such as SO_x, CO₂, and HCl.

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Notes

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