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Clean hydrogen from water: emerging technologies for a sustainable energy future

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Hydrogen has become more and more accepted as a key component in the transition to cleaner energy systems since it provides a high energy output without producing carbon on site. Although this is a potential, the majority of hydrogen is produced through fossil-based processes. Low-carbon hydrogen production pathways such as water electrolysis are increasingly attracting attention; however, their large-scale deployment is influenced primarily by electricity demand, system efficiency, and water quality requirements rather than bulk water consumption itself. Even more clean production paths like electrolysis are usually reliant on high-quality freshwater, particularly in proton exchange membrane (PEM) systems where high-purity feedwater is necessary to prevent membrane degradation and catalyst poisoning. Although the actual water consumption associated with electrolysis is relatively modest compared with many industrial processes, there is a shift in focus to use of alternative water sources to improve resource circularity and reduce dependence on high-purity freshwater in water-stressed regions. The concept of all water to hydrogen is to combine water treatment with hydrogen production enabling the use of various forms of water as a clean energy feedstock. This will not only alleviate pressure on freshwater resources, but also encourage the use of wastewater in a circular economy structure. In this aspect, freshwater, seawater, wastewater, and grey water are all under consideration as means of producing hydrogen. This review examines the connection between water and hydrogen generation, highlighting the necessity to shift towards systems that are not based on freshwater and focus on less utilized and more accessible water resources. The review further emphasizes that the dominant techno-economic challenge in electrolysis remains the high energy requirement associated with water splitting, while water quality mainly affects electrolyser durability and long-term operational stability. There is an indication that given the right pre-treatment techniques, long-lasting materials to stop corrosion, and enhanced electrochemical technologies, various water sources can be utilized successfully to generate hydrogen. Production of hydrogen using saline and wastewaters is also a viable path forward in solving the energy and water crises at the same time. This article unites the latest advancement and technology that contribute to the idea of All Water to Hydrogen. Its unique contribution is its analysis of various water sources in one framework in particular, the wastewater systems, their treatment requirements, performance efficiency, and scaling-up factors. The review offers a clear way to apply this concept to the real-world applications by linking hydrogen production and sustainable water management.

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1 Introduction

1.1 The global hydrogen economy and clean energy transition

Hydrogen is also starting to be viewed as a pillar of the move towards a cleaner, lower carbon, and more resilient energy system in the world. The quick pace of technological advancements is enhancing the viability of hydrogen production using renewable and alternative resources, as well as developing approaches to its storage, transportation, and end-use. Hydrogen contains a high-energy density as a flexible carrier of energy and produces no carbon emissions at the point of use, which makes it have a high potential to decarbonize hard-to-abate sectors, including transportation and power generation, refining, and heavy industries such as steel and chemicals. Over the last few years, with a major push, there has been a focus on the development of cost-effective and scalable production pathways, including water electrolysis using renewable electricity, biomass conversion, and waste-to-hydrogen pathways. Such methods not only decrease the reliance on fossil fuels but also help in diversifying and securing energy. Moreover, the development of storage technologies such as compressed gas, liquefied hydrogen, and solid-state carriers is also assisting with the problem of low volumetric energy density of hydrogen and its difficulty to handle. The use of fuel cells and hydrogen-based energy systems is also broadening its applicability in stationary and mobile energy applications.

In spite of these bright prospects, there are a number of serious issues. The high cost of production, infrastructure, energy wastes in conversion processes and safety are still a setback to the extensive uptake. This requires extensive investment, enabling policy frameworks, and standard regulations to speed up the commercialization and deployment. Also, it is an important research objective to enhance the overall efficiency and the lifecycle sustainability of hydrogen systems. Meanwhile, the combination of hydrogen technology with renewable energy systems are transformational opportunities. The excess renewable energy could be processed to hydrogen by power-to-gas technologies, allowing balancing in the energy grid and long-term energy storage. In addition, the use of waste materials like wastewater, agricultural materials, and food waste to generate hydrogen will contribute to the recovery of resources and minimize environmental pollution. These combined strategies also fit into the principles of the circular economy, reducing the waste, increasing resource utilization, and producing higher value products out of other unused resources. In the future, the hydrogen economy will be an important part of meeting global climate targets and sustainable development goals. Further innovation, interdisciplinary cooperation, and investments will play a vital role in breaking the current barriers and realizing the full potential of hydrogen as a clean and sustainable energy solution.[1]

Hydrogen is gaining popularity as an all-purpose, low-emission energy carrier with the potential to underpin a diverse spectrum of applications in a variety of sectors. It can be used in the power sector by deploying in fuel cells to produce electricity economically, as used with natural gas as a co-fuel to reduce emissions, or by direct combustion both in gas turbines and in internal combustion engines, to provide routes to near-zero or zero-carbon power generation. It is also useful to stabilize grids in the presence of renewable energy sharing a high percentage because of its capacity to supply dispatchable energy. Hydrogen is an important factor in the transportation industry, where fuel cell vehicles (FCVs) have greater driving range and can be refuelled much faster than battery-electric vehicles (BEVs). These strengths make hydrogen a viable option in heavy-duty and long-haul vehicles like freight and public buses, trains, and maritime transport. In addition, hydrogen-based fuels like ammonia and synthetic hydrocarbons are becoming prospective aviation and shipping solutions with direct electrification being difficult.[2] Hydrogen is an important feedstock in industrial operations besides being the source of energy and mobility. It is already extensively applied in petroleum refining, ammonia, and methanol production but its application is also broadening in low-carbon steel production *via* direct reduced iron (DRI) processes and other hard-to-abate industries. By substituting fossil-based hydrogen with green hydrogen in these industries, carbon emission in the world can be greatly cut.

Hydrogen is also a good prospect in residential and commercial heating, either mixed with natural gas or used in hydrogen-ready boilers or fuel cell-based combined heat and power (CHP) systems. This shift would help decrease building emissions which comprise a significant portion of world energy usage. Powerful policy frameworks, global partnerships, and massive investments are the forces behind the global shift to a hydrogen economy. Over 40 nations have launched national hydrogen plans, with funding to support research, pilot projects and infrastructure, including hydrogen pipelines, storage and refuelling stations. Cross-border hydrogen trade and public-private partnerships are also on the rise, especially in areas that are also targeting to be major exporters of green hydrogen. A key benefit of hydrogen is that it enables storage of energy, as well as sector coupling. It has the ability to store surplus electricity produced by intermittent renewable sources such as solar and wind through electrolysis and thus converted to chemical energy, which can be stored, transported and eventually converted to electricity or used as fuel. This potential increases grid flexibility, decreases renewable curtailment, and resilience of the energy system. Nevertheless, a number of issues have to be overcome to make the potential of hydrogen a reality. They are high production costs, energy wastage during conversion processes, infrastructure constraints, and storage and transport safety issues. The most important of these is the fact that the traditional electrolysis uses high-purity freshwater, which is a serious sustainability issue, especially in water-deprived areas. As a way of addressing this weakness, more efforts are being focused on the use of other water sources like seawater, wastewater, and greywater as sources of hydrogen. Emerging technologies such as direct seawater electrolysis and advanced pre-treatment systems are also designed to reduce freshwater demand without compromising efficiency and longevity of the system. Moreover, the possibility to combine hydrogen production and wastewater treatment plants are a two-way gain of energy production and resource re-use, which is consistent with the principles of the circular economy.[3] Although alternative water resources provide opportunities for sustainable resource recovery and circular water management, they should not be interpreted as the primary limiting factor in hydrogen production systems. At present, the major limitation of electrolytic hydrogen production is not the availability of water itself, but the high energy consumption associated with water splitting. The decomposition of water molecules during electrolysis requires substantial electrical input, which significantly increases operational costs and limits large-scale commercial implementation.[4] Consequently, conventional electrolysis has historically been restricted to specialized applications where high-purity hydrogen is essential, such as in nuclear and aerospace industries. To address this challenge, extensive research has focused on improving the energy efficiency of hydrogen production technologies through advanced electrocatalysts, optimized electrolyzer configurations, and high-temperature electrolysis systems that reduce the thermodynamic energy demand of water decomposition. These developments are expected to enhance the economic feasibility and sustainability of green hydrogen production, particularly when integrated with renewable energy resources.[5] In the future, the further evolution of the electrolyser technology, integration of renewable energy, catalyst development, and optimization of the system should lead to a decrease in costs and enhancement of efficiency. These innovations will be instrumental in making hydrogen a foundation of a sustainable, low-carbon energy future, coupled with favorable policies and global collaboration.

1.2 The water–hydrogen nexus and need for alternative water sources

Water and energy systems are inherently connected and one cannot run well without the other. Water is essential in the production of energy such as cooling in thermal power plants, hydropower generation, and fuel production, and the energy is also essential in pumping, desalination, treatment, and distribution of water, wastewater collection, and purification. This interdependence is termed as the water-energy nexus, where both resources need to be dealt with in concert and in a coordinated approach. As shown in Fig. 1 water, energy and

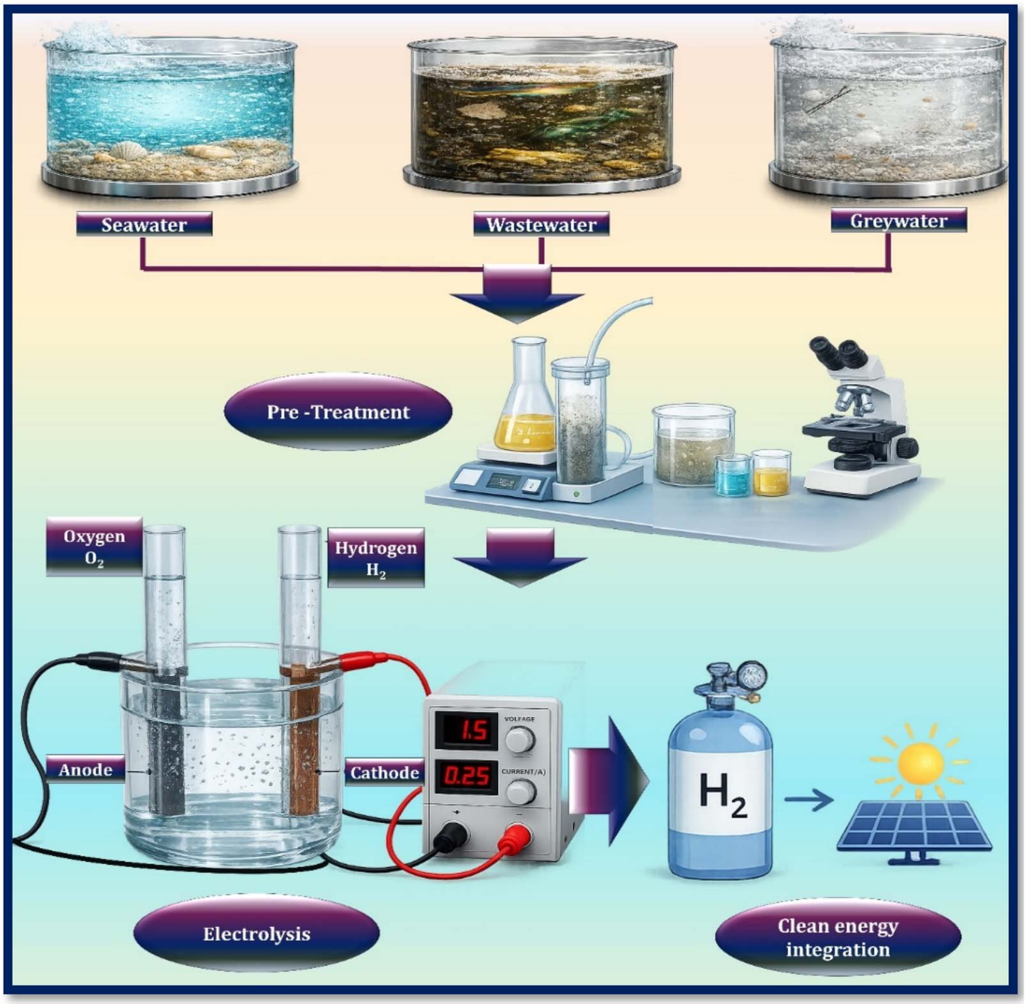

Fig. 1 Integrated framework of water sources and hydrogen production routes.

environmental sustainability are a closely intertwined system that supports the economic growth, stability of the ecosystem and human welfare.

The relationship between the water and energy sectors is strong so that inefficiencies or disruptions in one sector can have a direct effect on the other. For example, energy-intensive water treatment processes can dramatically raise both operational costs and carbon emissions, whereas water scarcity can restrict energy production (especially in water-dependent technologies like thermoelectric and hydropower). Accordingly, water and wastewater infrastructure should be designed and operated with energy efficiency as a consideration, utilizing advanced technologies such as energy recovery systems, smart monitoring, and decentralized treatment methods. Likewise, energy planning should consider water availability, water quality, and competing demands for water from agriculture, industry, and domestic uses. The increasing adoption of renewable energy sources introduces both opportunities and challenges to the nexus. Technologies such as solar or wind power generally require less water than conventional sources of energy, thus providing ways to reduce the stress on water. However, emerging hydrogen production technologies such as water electrolysis require reliable water quality and appropriate resource management, encouraging interest in alternative water sources such as seawater and treated wastewater for sustainable long-term deployment. Although electrolysis requires water as a feedstock, water consumption in electrolysis is relatively low, approximately 0.8 dm^3 per 1 m^3 of hydrogen produced;[6] therefore, global water demand is not considered a major limiting factor for hydrogen scale-up. However, water quality becomes particularly important for proton exchange membrane (PEM) electrolysers, which require high-purity feedwater to prevent membrane degradation and catalyst poisoning. Alkaline electrolysers are comparatively more tolerant to water impurities, although pretreatment remains necessary to ensure long-term operational stability. In practical systems, the dominant challenge is not water quantity itself, but the high electrical energy demand associated with water splitting and maintaining suitable water quality for durable electrolyser operation.[7]

Water resource management is becoming increasingly important because of population growth, climate change, urbanisation, and industrial expansion. These pressures highlight the importance of improving water reuse, treatment efficiency, and resource recovery within integrated water–energy systems. In the context of hydrogen production, alternative water sources such as seawater and treated wastewater are being investigated primarily to support circular resource utilization and reduce dependence on high-purity freshwater in regions facing water stress.[8] However, the principal challenge in water electrolysis remains the high electrical energy requirement associated with water splitting, while water quality mainly influences electrolyser durability, membrane stability, and long-term operational efficiency.[9]

Currently, over 40% of the global population faces water-related challenges, while 700+ million people do not have reliable/safe drinking water to meet their daily needs. As Fig. 2 shows, large amounts of wastewater produced by domestic, industrial & agricultural sectors are discharged into natural waters without treatment, contaminating those ecosystems and threatening human health. Climate change, urbanization, industrial expansion, and population growth continue to place pressure on regional freshwater resources. These trends highlight the importance of improving water treatment, reuse, desalination, and integrated water management strategies to support sustainable industrial development, including emerging hydrogen production systems. Extreme weather patterns caused by climate change (seasonal fluctuations in precipitation, long-term droughts, and other severe weather events) are destroying traditional water supply systems and impacting global food supply. Further compounding these

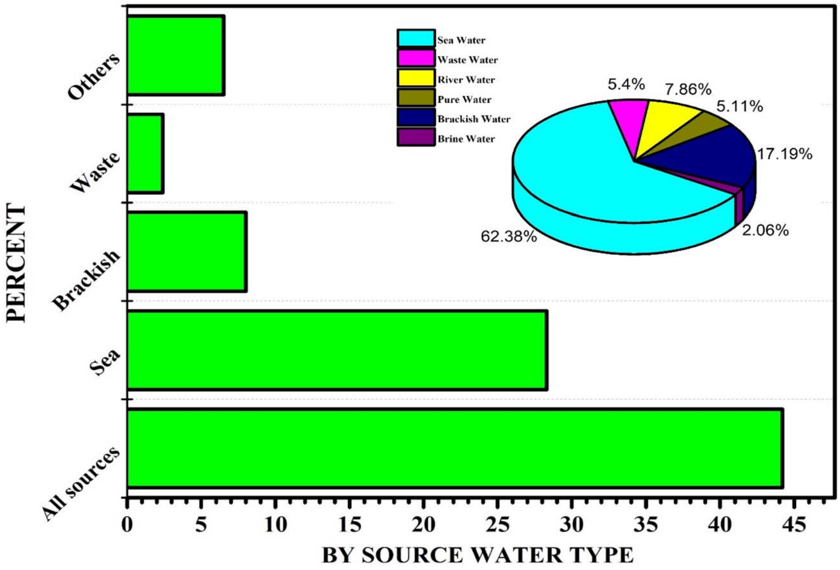

Fig. 2 Distribution of water types and their availability, adapted from ref. 11 with permission from IOP Publishing, © IOP Publishing 2021, distributed under the Creative Commons Attribution 4.0 International License (CC BY 4.0).

challenges is the over-extraction or overuse of groundwater in regions where it is relied upon as an emergency water supply at unsustainable levels, thus resulting in declining groundwater levels and/or the deterioration of groundwater quality.

Technological advances are becoming more important in solving these issues. Membrane technologies, forward osmosis (energy-efficient osmotic processes), as well as "hybrid" desalination processes will make the treated water process more efficient and cheaper. New, decentralized wastewater treatment and reuse systems are being promoted as sustainable solutions, particularly in urban and industrial areas. Wastewater is now considered an asset, instead of a liability, and can possibly be reused in irrigation, industries and, after treatment, even as drinking water. Integrated water resources management (IWRM) methods are necessary to bring about a coordinated development and management of the multiple interrelated areas of water, land, and other related resources. Developing policy frameworks and governance structures and involving local communities are critical to providing equitable distribution of water, as well as long-term sustainability of water resources. Raising public awareness, including individuals changing their behavioural patterns, adopting water-efficient practices (*i.e.* rainwater harvesting, smart irrigation systems, reusing water) can greatly reduce total water consumption. In totality, addressing the issue of global water scarcity, requires an integrated and multi-dimensional method that includes advances in technology, policy intervention, protecting the environment, and being socially responsible. Adopting circular principles of water economy and creating incentives for innovating in water treatment and reuse can help us get to a more secure, sustainable, and resilient water future.[10]

Fig. 3 shows the renewable energy technologies are expanding rapidly throughout the world, while at the same time, water availability is decreasing significantly, which again puts a spotlight on the need for suitable water quality and efficient system integration for green hydrogen production. This has increased interest in developing integrated water management and energy-efficient treatment strategies that can maintain electrolyser durability while minimizing additional processing costs. Hydrogen is recognised as a very versatile energy carrier that is also clean; as such, it has an important role to play in the shift to low-carbon energy systems. In other words, hydrogen produces only water as a result of being burned, therefore it emits no greenhouse gas or harmful pollutants. This makes hydrogen a preferred alternative to fossil fuels. One important consideration for large-scale hydrogen production is maintaining suitable water quality for electrolyser stability and membrane durability, particularly in PEM-based systems. In reality, only certain electrolyser technologies, particularly proton exchange membrane (PEM) electrolysers, require highly purified water to avoid membrane degradation, catalyst poisoning, and conductivity losses. Alkaline and high-

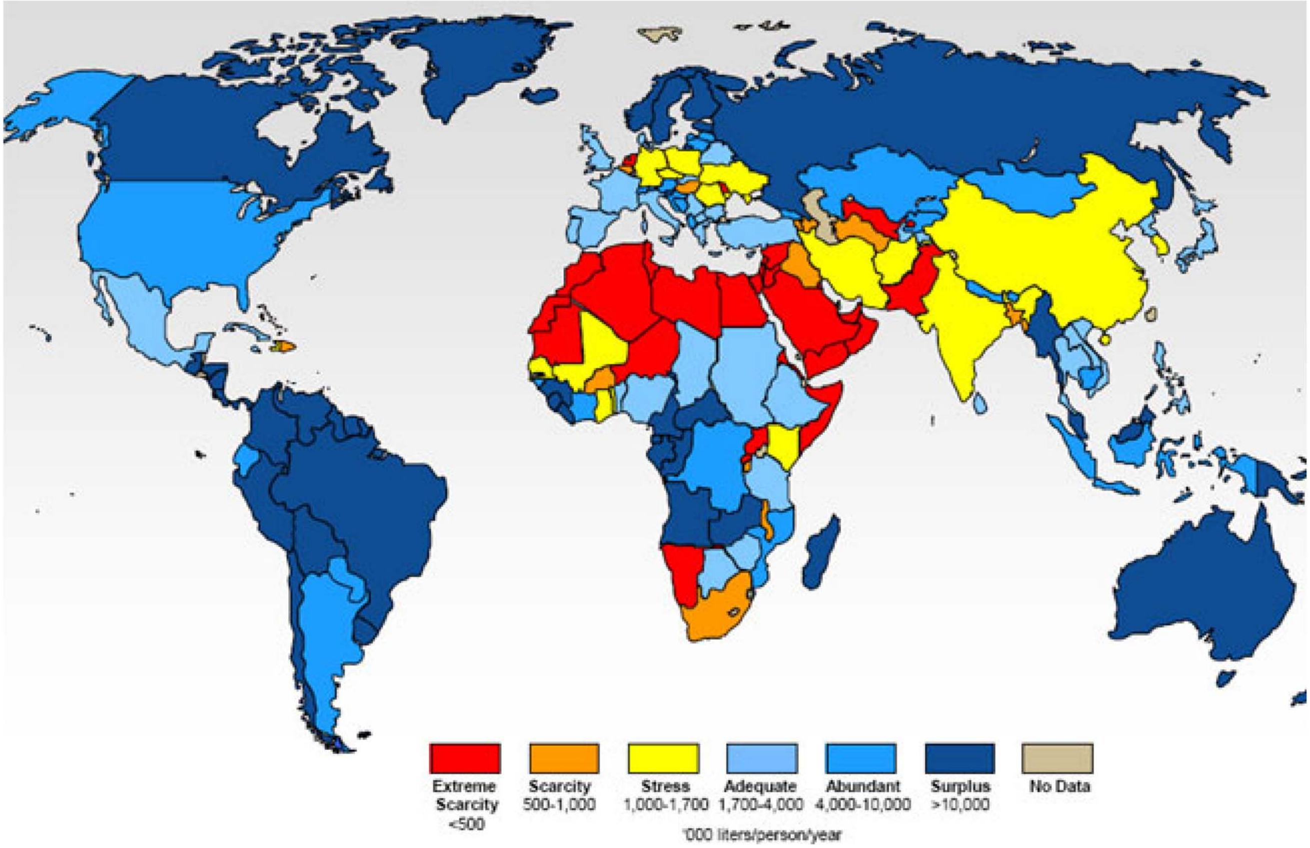

Fig. 3 Worldwide distribution of water scarcity from ref. 12 with permission from Springer Nature © 2016 under the Creative Commons Attribution 4.0 International License (CC BY 4.0).

temperature solid oxide electrolysis systems are generally more tolerant to variations in water quality, thereby reducing the dependence on ultrapure feedwater.[13] As many freshwater sources are already under stress from overuse or pollution, they cannot meet the increasing demand for water in regions where hydrogen production is being developed. Although water demand for electrolysis is comparatively modest, the purification requirements associated with some electrolyser technologies may increase system complexity and operational cost. There are now many alternative water sources being examined as potential substitutes for freshwater; these sources do not reduce the availability of drinking water or agricultural water supplies. Seawater, which covers approximately 71% of the Earth's surface, is also plentiful and essentially an inexhaustible resource. Electrolysis of seawater represents a viable means of producing hydrogen without depleting groundwater supplies while also allowing for larger-scale decentralized hydrogen production. For coastal countries, this method of producing hydrogen will allow the combined use of water from the ocean and renewable energy to generate hydrogen. The motivation for exploring alternative water sources is therefore not solely driven by absolute water scarcity, but also by the broader objective of improving resource circularity, reducing competition with potable water supplies, and integrating hydrogen production with wastewater treatment and industrial water reuse systems.

Nonetheless, there are also technical obstacles associated with water electrolysis for saltwater directly. From a thermodynamic perspective, one of the major challenges in direct seawater electrolysis is the competition between the oxygen evolution reaction (OER) and the chlorine evolution reaction (ClER). Under saline conditions, chloride ions can undergo oxidation to chlorine species, particularly under acidic or highly oxidative environments. Therefore, the development of highly selective electrocatalysts that preferentially promote OER while suppressing chlorine evolution is essential for achieving efficient and durable seawater electrolysis systems.[14] Dissolved salts in solution (chloride ions in particular) can cause side reactions to occur such as the production of chlorine gas during the hydrogen gas production process. In return, these side reactions will lead to decreased hydrogen gas production efficiencies because they will produce less hydrogen gas than would otherwise occur as well as cause damage to electrodes and components of the entire electrolysis system. Electrodes will degrade, membranes will become fouled, membranes will scale, *etc.*, all creating problems that have to be dealt with to enable long-term continuous operation of the system. Therefore, substantial efforts have been committed to investigating advanced catalysts, corrosion resistant materials and selective membranes that will improve performance while minimizing or eliminating competing reactions. Innovative design ideas for systems have also been investigated in order to improve the feasibility of utilizing seawater as an alternative source of water for electrolysis. Examples of new systems include hybrid systems utilizing both desalination and electrolysis processes, indirect seawater splitting by using intermediate streams that have been purified before splitting into hydrogen and oxygen, and specialized electrolyzers designed for use in high salinity conditions. Nanomaterials and surface engineering techniques developed in recently completed research appear to have the potential to improve selectivity of the oxygen formation reaction compared with the chlorine gas formation reaction thereby increasing the overall effectiveness of the complete electrolysis system. Recent catalyst research has therefore focused not only on improving hydrogen evolution activity, but also on lowering polarization resistance, suppressing parasitic reactions, and replacing expensive noble metals with earth-abundant alternatives such as NiFe layered double hydroxides, Mo-based catalysts, transition metal phosphides, sulfides, and CeO_2-modified materials. These developments are intended to improve long-term stability, reduce energy consumption, and enhance scalability under realistic operating conditions.[15]

Combining seawater electrolysis with renewable energy sources increases the promise of seawater electrolysis as a sustainable solution to many energy and environmental challenges today. Offshore wind farms and floating solar systems can provide the electricity needed for electrolysis to take place on-site island-based or on the ocean without the need for expensive transportation infrastructure. This offers opportunities for storage solutions, grid stability, and the production of green fuels (*e.g.*, ammonia and methanol). The hydrogen produced through seawater electrolysis can aid in the decarbonisation of sectors that are challenging to decarbonise (shipping, aviation and heavy industry). In addition to offering economic and environmental benefits, hydrogen produced using seawater could alleviate pressure on freshwater ecosystems and promote circular, resource-efficient energy systems. Furthermore, hydrogen produced from seawater supports the achievement of the global sustainability agenda by providing clean energy access, lowering carbon emissions, and developing coastal and island economies.[16] In summary, while there are still some technical and economic challenges with seawater electrolysis, it is poised to be a key part of the future of hydrogen production. Continued advancements in material science, systems engineering and renewable energy integration will be crucial to realising its full potential. By converting a plentiful, natural resource into a clean energy carrier, seawater electrolysis may underpin a secure and sustainable global energy future.

Special emphasis is placed throughout this review on the relationship between energy efficiency, catalyst durability, feedwater quality, and system-level integration, since these factors collectively determine the practical feasibility of sustainable hydrogen production technologies. This review is structured into four main themes: (i) hydrogen production pathways, (ii) wastewater-to-hydrogen systems, (iii) pretreatment and material limitations, and (iv) scale-up challenges and techno-economic considerations.

2 Water sources for hydrogen production

The Table 1 below list several types of water sources used for producing hydrogen and their specific characteristics:

Table 1 Comparative properties of different water sources (salinity, COD, key ions)

S. no	Water source	Availability	Salinity/TDS (mg L^{-1})	COD (mg L^{-1})	Key ions/impurities	Notes/challenges for H_2 production	Ref.
1	Freshwater	Rivers, lakes, and groundwater; uneven global distribution	<500	<20	Ca^{2+}, Mg^{2+} (trace)	Requires high purification energy	18
2	Seawater	Abundant (~97% of Earth's water)	35 000–45 000	50–200	Na^+, Cl^-, Mg^{2+}, Ca^{2+}, SO_4^{2-}	Corrosion, scaling, ClER competing with OER	19
3	Industrial wastewater	Refineries, textiles, food, chemicals	1000–10 000	500–3000	Cl^-, SO_4^{2-}, Cu, Fe, Zn, Pb, hydrocarbons	Toxic metals poison catalysts; high pre-treatment needed	20
4	Greywater	Household activities (laundry, kitchen, bathing)	200–1500	100–800	Surfactants, Cl^-, PO_4^{3-}, trace metals	Low salinity, but surfactants cause electrode fouling	21

freshwater, seawater, industrial wastewater and greywater all have different chemical compositions. These water sources vary dramatically regarding salinity, organic matter content, presence/absence of dissolved ions, suspended solids, and possible hazardous wastes from metals or chemicals. Therefore, the treatment or pre-treatment to facilitate electrolysis or hydrogen production will also differ by these types of water sources and intensity. For example, high-purity water is primarily required for membrane-based electrolysis systems, where ionic contaminants can accelerate membrane degradation, catalyst poisoning, and scaling. Consequently, water quality management is more closely associated with system durability and operational stability than with absolute water availability.[17] However, in seawater, the high concentrations of salts (primarily chlorides) present create the potential for corrosion and undesirable side reactions on electrolytic electrodes, thus requiring desalting or other advanced purification methods. The treatment of industrial waste requires many different kinds of treatments; *i.e.*, filtration, chemical or biological treatment of organic/inorganic pollutants/oils/toxic materials. Even though greywater is not as contaminated as industrial wastewater, it still contains soap/detergents/residual organics that must be treated to provide efficient/stable hydrogen production. Differences between types of water and respective quality affect the water treatment technology choice, operational costs and system design specifications directly. It is important to understand these differences when attempting to optimize resource usage and establish sustainable hydrogen production using non-traditional/diverse source waters.

2.1 Fresh water

Most of the Earth is oceanic, comprising approximately 71% of the Earth's surface area; hence approximately 29% is land-based. Yet only a limited amount of the Earth's water can be consumed by humans or used for industrial purposes, with freshwater accounting for approximately three percent of the world's total water supply (or about 1/20th of a percent of the Earth's total). Of the Earth's total freshwater supply, something less than 0.06% is accessible to humans at any time. Most of the freshwater supply on the planet is either contained in glaciers, ice caps at the poles, or located in deep aquifers underground. The imbalanced distribution of freshwater resources worldwide is increasing the stress placed on those portions of the global freshwater supply that are accessible. As a result, managing and using the freshwater supply that is available to humans effectively is critical for both the continued survival of humans and the maintenance of ecological balance. Body of water on the Earth's surface (*e.g.*, lakes and rivers) form an integral part of the global hydrologic cycle while also providing water for multiple purposes, including agricultural, industrial, and domestic. Lakes are important reservoirs of surface freshwater, containing approximately 87% of all accessible surface freshwater, with only about 2% found in rivers; nevertheless, lakes are relatively stationary bodies of water, while rivers provide dynamic channels for moving water over large areas of land. For this reason, rivers are particularly important components of irrigation systems, municipal water supply systems, and ecosystems, since they continually supply water to those systems. In addition, rivers support biological diversity, help control local climate, and play a role in cycling nutrients around the environment, contributing to their overall ecological importance.[22,23]

For hydrogen electrolysis, feedwater quality is an important operational parameter because dissolved salts, organic compounds, and suspended solids can reduce membrane lifetime, poison catalysts, and increase scaling within electrolysers. Consequently, pre-treatment processes such as filtration, ion exchange, softening, and reverse osmosis are often required before electrolysis, particularly for PEM systems. Input water quality therefore strongly influences system efficiency, operational stability, and electrode durability.[24] In this regard, Table 2 summarizes physical, chemical, and biological pre-treatment methods that are compatible with different electrolysis technologies and electrode materials. These processes remove impurities including salts, organic substances, and suspended solids, thereby improving electrolysis performance and extending system lifetime. However, the additional energy consumption and operational costs associated with water purification must also be considered when evaluating the overall sustainability and economic feasibility of hydrogen production from alternative water sources such as seawater, wastewater, and brackish water.[25]

2.2 Sea water

The oceans in Fig. 4 contain almost 97% of the planet's total water supply. However, because of the relatively high sodium chloride (NaCl) salt concentrations ($35\ \mathrm{g\ L^{-1}}$) within the oceans, the oceans cannot be directly used for potable (drinking) water or for many uses in industry. Ocean water is therefore poised to be a very abundant and reliable alternative freshwater supply, especially considering the strain being placed on global freshwater supplies from population growth, urbanization and climate change, with many coastal and arid regions having few options for freshwater supplies other than seawater. The use of seawater is especially relevant in the context of producing hydrogen sustainably, where access to high-purity water and appropriate treatment infrastructure becomes an important operational consideration. In order for seawater to be an acceptable source of water for processes like electrolysis, desalination or pre-treatment must take place. Conventional desalination processes such as reverse osmosis or thermal distillation are the most common methods of removing salts and other impurities from seawater. Compared to conventional methods for producing hydrogen through electrolysis, current methods are energy-intensive to run, which leads to higher costs for hydrogen production overall. Furthermore, discharging highly concentrated brine, which contains residual chemicals from the seawater, presents serious environmental risks such as disrupting marine ecosystems and raising coastal water salinity. Therefore, while seawater is generally considered a good source of hydrogen, other methods have been explored that may reduce processing costs and energy consumption. These methods include using electrolysis to directly convert seawater into hydrogen. This process has not been widely used due to several technical issues associated with using seawater: corrosion of electrodes, competing side reactions, like generating chlorine gas, and membrane breakdown due to chloride ions and other impurities found in seawater. To overcome these problems, researchers have created advanced pre-treatment technologies (*e.g.*, filtration, ion exchange, addition of chemicals, biological treatment) to enhance the water quality before performing electrolysis.[29]

In addition, the design of new catalysts and new types of electrode materials is a key factor in improving both the efficiency and the lifetime of sea water electolysis systems. Development of materials resistant to corrosion, selective catalysts, and protective coatings are being evaluated for their applicability in reducing unwanted reaction rates and increasing system longevity. There are opportunities to provide systems that integrate the use of renewable energy sources such as solar and wind with sea water desalination and electrolysis to reduce both the carbon footprint associated with hydrogen production and to provide more sustainable hydrogen production processes. A summary of the different types of pre-treatment methods, electrolysis methods and electrode materials including the advantages, disadvantages, and the suitability of each of them for sea water-based hydrogen production is provided in Table 3. Overall, while still faced with numerous challenges, these advancements illustrate that while there are still significant technical and economic obstacles to overcome, seawater represents a strong candidate to develop into a viable resource for producing hydrogen in large quantities on a sustainable basis if supported by the correct technology and responsible environmental stewardship.

2.3 Industrial wastewater

Across many diverse sectors of the economy, including manufacturing, thermal/renewable energy production, agriculture, mining, and oil and gas, water is a critical resource for industrial operations. Therefore, sustainable use of water has

Table 2 Comparative summary of catalysts and operating conditions for freshwater electrolysis

S. no	Sector	Pre-treatment	Type	Electrode	Performance	Challenges	Ref.
1	Lab/research	DI water + KOH	AWE	NiFe-LDH/Ni	260 mV; stable >100 h	Impurities, oxidation, scaling	26
2	Industrial/pilot	Soft filtered water	PEMWE	IrO_2–RuO_2/Pt	>80% eff.; >99.9% purity	High cost, feed limits	27
3	Demo plant	Filtration + ion exchange	AEM	NiFeOx/Co_3O_4	2.1 V; 70%; >1000 h	Membrane instability	28
4	Advanced R&D	DI + KOH + O_2 removal	SOEC	Ni–YSZ/LSM	η > 90%; high T	Thermal stress, corrosion	28

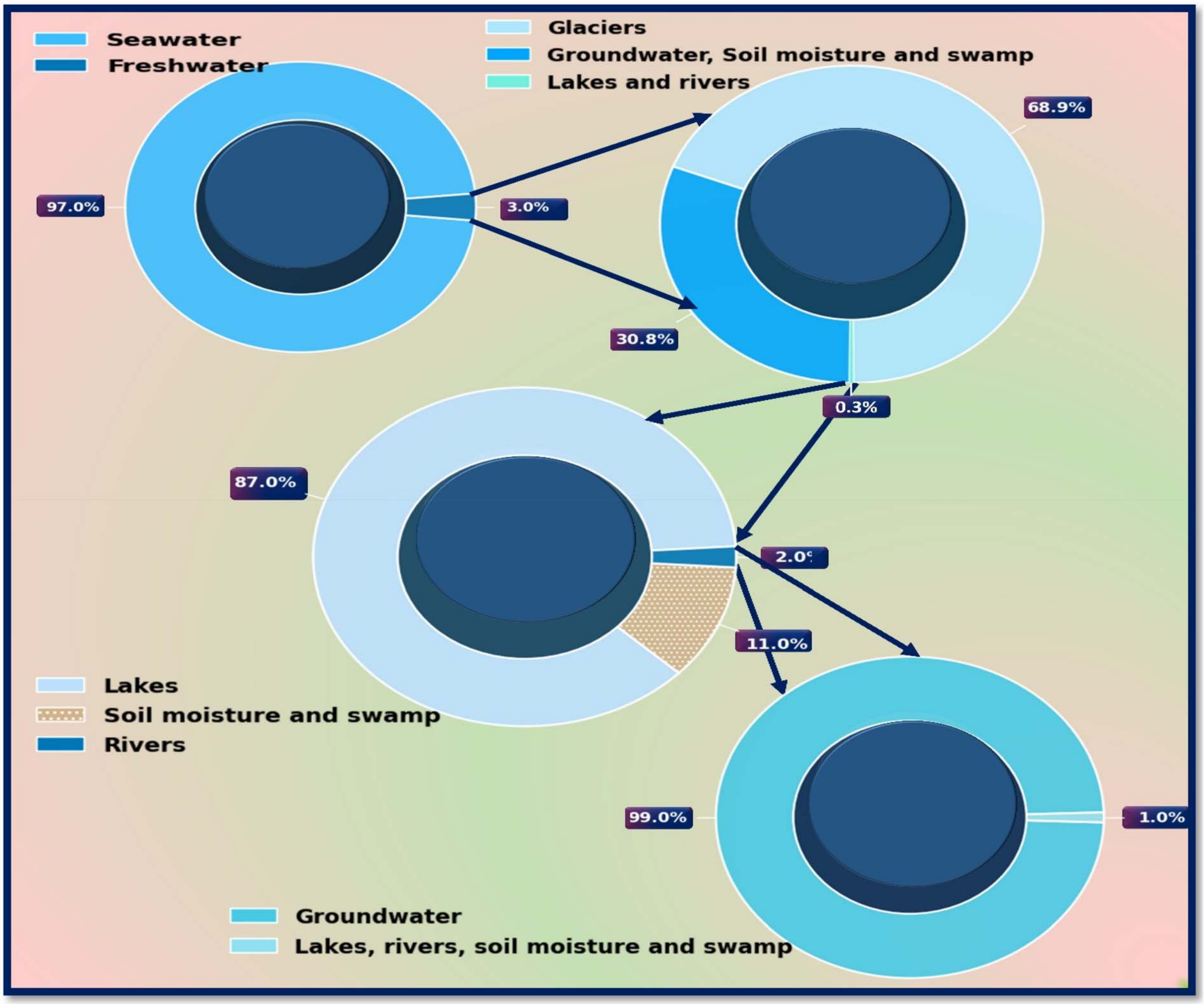

Fig. 4 Distribution of Earth's water resources by source, volume, and accessibility.

Table 3 Recent advances in alkaline and seawater electrolysis: catalyst design, performance, and limitations

S. no	Sector	Method	Type	Catalyst	Performance	Challenge	Ref.
1	Lab/industrial	Purified + 1 M KOH	Alkaline	CuO/Cu foil	270 mV, >90% FE	Purity, corrosion	30
2	Seawater	Filtration + KOH	Alkaline	Au–Gd–Co_2B@TiO_2	510 mV, durable	Complex synthesis	30
3	Seawater	Direct use	Alkaline	NiOOH/$Ni(OH)_2$	400 mV, 168 h stable	Complex fabrication	31
4	Seawater	+Hydrazine	Hydrazine-assisted	Co/N-carbon	0.557 V, low energy	Toxic, costly	32
5	Seawater	Alkaline adj.	SOR-assisted	NiFe-LDH/$FeNi_2S_4$	1.05 V reduction	Sulfur management	33

become an essential goal for companies looking to balance their productivity with their commitment to the environment and long-term sustainability. Increased pressure to comply with regulations, growing concerns over the availability of fresh water, and the need to reduce cost are driving many companies to implement more advanced methods of managing and recycling water.[20] The treatment and safe disposal of industrial wastewater is one challenge that is particularly pressing for companies; hence, they are increasingly using an integrated approach that employs physical/chemical/biological wastewater treatment processes (often in a hybrid configuration) to improve total process efficiency. Industrial effluent is composed of a variety of constituents that exhibit a great deal of variability in quantity and quality based on multiple sources and various conditions that can occur at these sources. This variability can make treatment of industrial effluent difficult – some of the common characteristics of industrial effluent include: high total dissolved solids (TDS) concentrations; increasing chemical oxygen demand (COD) levels; high chloride concentrations; toxic levels of heavy metals such as Pb, Cd, Cr and Ni; large quantities of petroleum hydrocarbons, oil and grease; suspended solids; and various refractory organic chemicals. In

Table 4 Recent advances in alkaline and seawater electrolysis: catalyst design, performance, and limitations

S. no	Sector	Pre-treatment method	Electrolysis type	Electrode/catalyst type	Key performance	Main challenges	Ref.
1	Pilot (150 L MEC)	Industrial sugar-based wastewater, filtration + conditioning	Microbial electrolysis cell (MEC)	Ni-foam cathode	19.07 ± 0.46 L H_2 m^{-2} d^{-1}; COD removal 40% over 80 days	Lower COD removal; economic viability of Ni-foam	35
2	Industrial process effluent	Acidification + minimal purification (reclaimed water)	Alkaline water electrolysis (AWE)	Standard AWE electrodes (lab-scale)	Stability extended from 8 h to over 300 h at 150 mA cm^{-2}; cost reduction 47%	Membrane contamination; feed variability	36
3	Review of electrochemical H_2 from wastewater	Various industrial wastewaters	Hybrid electrochemical oxidation + H_2 production	Earth-abundant electrocatalysts	Hydrogen production cost ~US \$6.37 per kg H_2 (for some routes)	Scalability; feedstock heterogeneity; techno-economics	37

certain industries such as petrochemical and textile industries, the presence of dyes, hydrocarbons, and persistent organic pollutants adds to the complexity of these treatment processes, making the need for a customized treatment strategy necessary rather than the application of a universal or "one-size-fits-all" treatment strategy, as summarized on Table 4.

Contaminants associated with water used to generate hydrogen *via* electrolysis create a number of technical challenges. Metal ions can adsorb onto the catalyst surface leading to reduced activity and expiring catalyst lifetimes. High concentrations of chlorides can facilitate competing reactions for chlorine generation and may lead to accelerated corrosion rates on electrodes and other components of electrolysis systems. Organic impurities and high (*i.e.*, > 1000 mg COD per L) COD concentrations can lead to the fouling of membranes, reduce ionic conductivity, and impede mass transfer, thereby reducing the efficiency of the electrolysis system while increasing maintenance needs. In addition, scaling and salt precipitation can adversely affect electrolyzer performance over extended durations. To mitigate these types of issues, advanced pre-treatment technologies are becoming more prevalent. Pre-treatment technologies currently being studied include membrane based processes (*e.g.*, ultrafiltration, nanofiltration and reverse osmosis), advanced oxidation processes (AOP), electrocoagulation, and various novel materials (*e.g.* activated carbon, biochar, nanomaterials) for adsorption. Promising wastewater treatment methods that utilize a hybrid of various wastewater treatment technologies, will remove both organic and inorganic contaminants from the wastewater to enable the treated wastewater to be used as a feedstock for hydrogen production. Furthermore, from a sustainability standpoint, using industrial wastewater as a feedstock for hydrogen production has a number of beneficial aspects, including, supporting circular resource utilization by simultaneously treating wastewater and generating hydrogen while potentially reducing demand for highly purified freshwater feedstocks; and reducing the amount of environmental pollution that are normally generated as a by-product of wastewater discharge. Additionally, by combining wastewater treatment with hydrogen production will increase resource efficiency, reduce the costs of production, and will contribute to decarbonization in many different industries. Due to these dual benefits of using waste as a viable energy source and facilitating the generation of clean energy, the implementation of industrial wastewater valorization has established itself as a critical pathway to support the development of sustainable hydrogen production systems.[34–38] However, the energy and economic costs associated with wastewater purification must be carefully balanced against the operational benefits of alternative feedstocks, since highly contaminated streams may require extensive treatment prior to electrolysis.

2.4 Greywater

The reuse of greywater provides a useful method (and a growing trend) in lessening the need for fresh water. Greywater is the water coming from all domestic sources, such as bathing and handwashing, laundry, and the kitchen. Greywater does not include the waste water from toilets (blackwater). Greywater makes up approximately 50–75% of the total household waste water, so the recovery and reuse of greywater can contribute to improved water resource efficiency in decentralized water management systems. The greywater stream contains many different chemicals (for example, fats, oils and greases, dissolved solids, organics and products from personal care and cleaning such as soap, shampoo, detergent and toothpaste) and has trace levels of many emerging micropollutants (for example, pharmaceuticals and personal care products) that could pose a concern to the environment or health if not treated properly. The physicochemical properties of greywater can vary substantially from household to household due to different activities and product use within each household. Total dissolved solids (TDS) generally range from 300 mg L^{-1} to 1500 mg L^{-1}, while chemical oxygen demand (COD) can be as low as 58 mg L^{-1} and as high as 2497 mg L^{-1}, and biochemical oxygen demand (BOD) can vary from 100 mg L^{-1} to 1850 mg L^{-1}. Electrochemical processes can negatively impact corrosion in part by promoting ClER alongside the electrochemical oxygen evolution reaction (OER) due to higher than average chloride concentrations (30–400 mg L^{-1}). Additionally, trace metals (*e.g.*, Fe, Zn, Cu, and Pb) generally present from plumbing systems and cleaning products can build up on catalysts (which may be catalytic surfaces) causing fouling, deactivation of catalysts, and changes to electrochemical performance. Additionally, suspended solids and colloidal materials increase the resistance of the systems; decrease the conductivity of the system; and cause fouling of membranes by filtration.

In addition to these properties, grey water recycling provides a number of challenges and opportunities. Greywater can be recycled and used for non-potable uses. When treated appropriately, greywater can be used for landscape irrigation, flushing toilets, cooling systems, and as an input for many industrial and electrochemical applications, including hydrogen production. To safely use greywater, greywater must be treated appropriately to reduce organic load, pathogens, and micropollutants in order to provide safety and reliability. Common greywater treatment technologies include chemical treatments (screening, sedimentation, filtration), biological processes (aerobic and anaerobic treatment systems, constructed wetlands), and advanced technologies such as membrane filtration, adsorption, and advanced oxidation processes. The main challenge associated with greywater recycling is that greywater composition is highly variable in nature, thus complicating design and operation of a recycling process. Surfactants and organic matter can cause foaming which could stop oxygen transfer in biological systems while scaling and fouling may occur from electrochemical and membrane-based systems. Furthermore, possible disinfection by-product formations could take place during treatment due to the presence of chloride ions resulting in the need to monitor and manage these occurrences carefully.[38] There must be an effective pretreatment method used along with a tailored treatment strategy to improve efficiency and longevity of systems. In terms of sustainability, the use of decentralized greywater treatment

Table 5 Comparative assessment of greywater electrolysis pathways for sustainable hydrogen production

S. no	Sector	Pre-treatment method	Electrolysis type	Electrode/catalyst type	Key performance	Main challenges	Ref.
1	Laboratory/pilot	Filtration + softening	Electrochemical hydrogen evolution	Ni-based electrode on foam support	Reported hydrogen production from enzyme or microbial assisted systems (requires further details)	Variable composition of greywater; surfactants & organics fouling electrodes	39
2	Urban scale MBR feed	Greywater after MBR biological treatment and membrane filtration	Microbial electrolysis cell (MEC) using treated greywater effluent	Carbon-cloth cathode, mixed catalyst	Demonstrated yields in pilot greywater treatment setups	Biological fouling, residual contaminants, scalability	40
3	Household/building	Primary filtration then electrochemical setup	Photo electrochemical/electrolysis hybrid	TiO_2/ZnO photoanodes + CuO/Cu cathodes	COD removal 73% with concurrent energy generation	Need adaptation from power generation to pure hydrogen; complex catalysts	41

and reuse systems is drawing interest because they can reduce the load placed on centralized wastewater infrastructures, decrease the amount of freshwater extracted, and also minimize the energy needed to transport water. When appropriately managed, greywater reuse can be critical to establishing sustainable circular water management systems, thus improving water security, decreasing environmental impacts, and improving resiliency in urban and rural areas.

Table 5 provides a full overview of how greywater varies and the impact that this causes to hydrogen production. It specifically discusses the need for adequate pre-treatment to remove contaminants such as organic material, surfactants, oils, suspended solids and dissolved salts that will negatively affect electrolysis systems. It identifies how the impurities in greywater affect the efficiency of electrolysers and gives examples of issues like electrode fouling, membrane deterioration and reduced catalytic activity. Table 5 also indicates the main operational and technical limitations of using greywater as a sustainable feedstock for producing hydrogen (*i.e.*, variations in the quality of greywater, more frequent maintenance is required and the need for robust, adaptable treatment technologies). Therefore, various measures must be taken to overcome these limitations if greywater is to be effectively used as a sustainable hydrogen feedstock.

3 Hydrogen production pathways from water

3.1 Electrochemical pathways

Green hydrogen is produced through water electrolysis, the use of electricity to separate water into H and O_2, which can be created from renewable resources, such as wind, solar and hydroelectric power. This electrochemical method is the basis for all sustainable hydrogen production processes and ultimately how to minimize carbon emissions. There are different technologies used for electrolysis depending on the type of electrolyte being used, the conditions under which your electrolysis occurs and what type of system is used for electrolysis. Alkaline water electrolysis (AWE) is the most established and used method of electrolysis and consists of using a liquid alkaline electrolyte such as potassium hydroxide (KOH). The main advantages of AWE technologies are long-term durability, cost effectiveness, and the ability to be deployed at very high volume and scale. However, AWE technologies typically operate at lower current densities and therefore can also respond relatively slowly to changes in renewable energy input, making them less desirable for dynamically changing renewable resources.

PEM electrolysis uses a polymer membrane as the electrolyte rather than a liquid electrolyte; consequently, it allows for the design of small systems and high current densities and must be designed to quickly respond to load fluctuations from renewable energy sources connected to the grid. These characteristics make PEM a good match to be integrated with intermittent renewable energy sources. PEM systems are costly because they require expensive noble metals (*e.g.*, Pt and Ir) as catalysts. SOECs operate at high temperatures (700–1000 °C), allowing for high electrical efficiency because they produce electricity using the thermal energy produced by the system. This makes SOECs attractive for industrial applications in which waste heat is available. However, there are challenges associated with material stability, thermal cycling, and lifetime durability that will keep SOECs from becoming commercially viable today. AEM electrolysis is a technology that attempts to combine the positive aspects of both AWE and PEM systems. A medium to dense and reactively uncovered generic electrochemical membrane, such as the proton exchange membrane (PEM), contains everything needed for the alkaline form of electrolysis (AEM). The key difference between them is the alkaline form, using non-precious metals, has the potential to lower the cost of manufacturing and installing an AEM electrolysis system. However, AEM technology continues to develop, including ongoing research to enhance the membrane's conductivity, chemical stability, and service life. All other components necessary for each respective technology will determine how productive an electrolysis system can be, including but not limited to: efficiency; cost; scalability; operational flexibility; and compatibility with renewable energy systems. Continued advances in materials science, catalyst development and system integration will likely improve the performance and economic feasibility of these respective technologies, resulting in further acceleration of the adoption of green hydrogen in the future energy market.[42]

3.1.1 Alkaline water electrolysis. The process of alkaline water electrolysis is a method in which water is split into hydrogen and oxygen ions by utilizing electrical energy in a strongly alkaline environment, typically made up of sodium hydroxide or potassium hydroxide. This is accomplished through two separate half–cell reactions: the hydrogen half–cell reaction at the cathode and the oxygen half–cell reaction at the anode. As shown in Fig. 5, at the cathode, H_2O molecules will gain electrons (are reduced) to make H_2 gas and OH^- ions. Hydrogen will leave the surface of the cathode forming bubbles, while OH^- ions travel through an electrically conductive porous separator or diaphragm to the anode. At the anode, OH^- ions will be converted to O_2 gas and H_2O molecules are formed to complete the electrochemical cycle.

Electrolytes are important for improving electrical conductivity through ionic means and also for providing stable operation of the cell. The separate chamber where two different gases (hydrogen and oxygen) are mixed is used as a safeguard to guarantee that these gases do not combine during operation. This will enhance the process safety and purity of products. Trimetallic (nickel/nickel alloy) or other transitional metals are typically used as electrodes since they exhibit stability (in alkaline solutions) and also because they have lower costs than other options (aluminum) when operated in alkaline electrolytic systems. Electrolytic conditions (temp, electrolyte conc., current density, pressure of gases) will affect both efficiency and rate of H_2 production. Normal alkaline electrolyzers are operated at temperatures of 60–90 °C. These operational temperature ranges have been determined to produce improved chemical reaction kinetics, and thus use less energy. However,

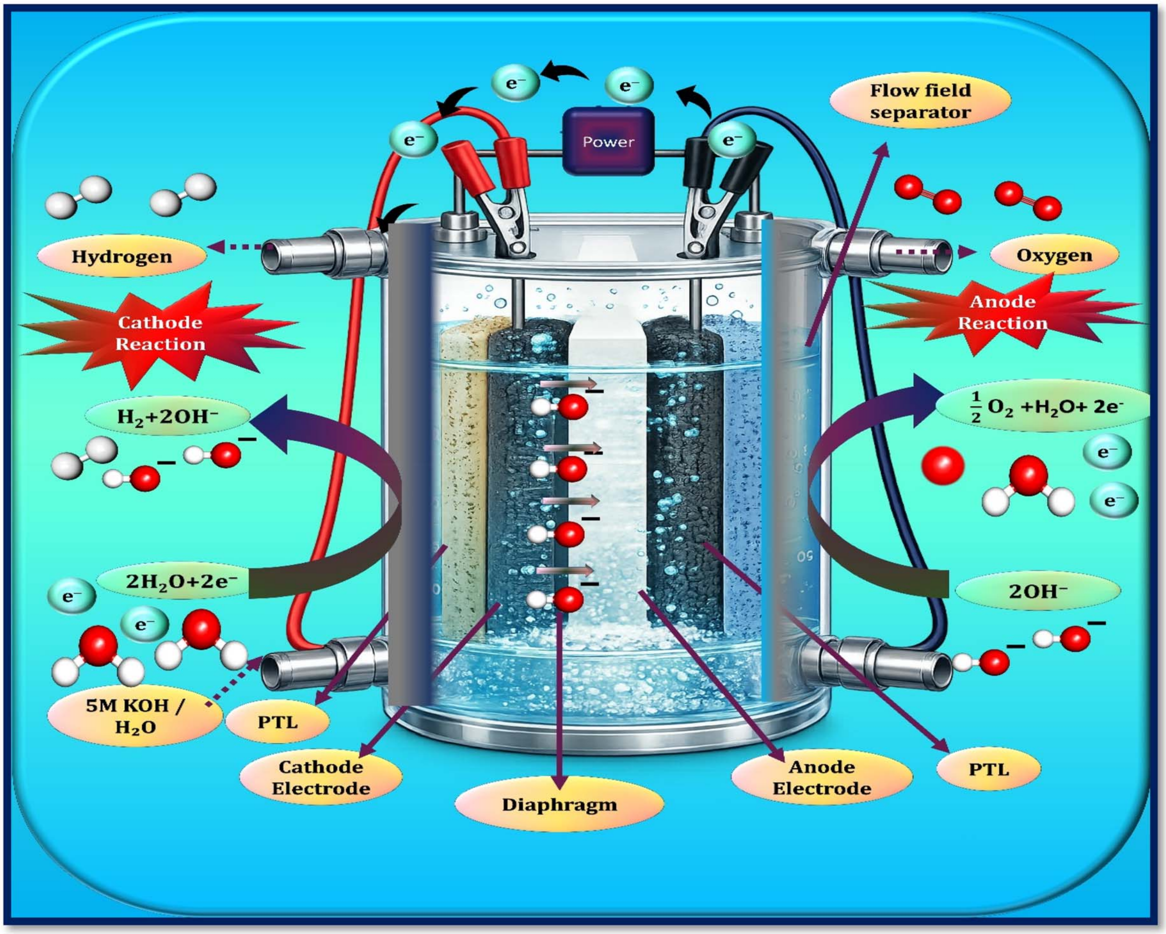

Fig. 5 Mechanistic representation of electrochemical reactions in alkaline water electrolysis systems.

alkaline electrolyzer systems are still limited in their ability to be operated in a high-performance manner due to gas crossover, electrode degradation, lower current density relative to more advanced systems, and other complications.

There has been considerable effort in identifying superior bifunctional electro-catalysts for accelerating the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) in alkaline solution. These catalysts include a wide variety of transition metal-based materials such as nickel, cobalt, iron, and their oxide, hydroxide, phosphide, and layered double hydroxide composites, that exhibit enhanced kinetics, reduced over potential, and improved efficiency when used as bifunctional HER/OER catalysts. Strategies involving nanostructured materials and engineered surfaces provide additional increases in active surface area and catalytic activity. Recent developments have also integrated alkaline electrolysis with renewable energy technologies (*e.g.*, solar and wind) for green and low-carbon hydrogen production. In addition, hybrid systems, advanced mem-bran-e materials, and optimized cell designs are under investigation to improve the durability, scalability and economic viability of alkaline electrolysis. A comparison of the various bifunctional catalyst systems and their electro-chemical performance can be found in Table 6, indicating that efforts are currently ongoing to improve alkaline electrolysis technologies.

3.1.2 Anion exchange membrane (AEM) water electrolysis. The concept for the use of proton exchange membrane (PEM) water electrolysis to overcome the limitations of alkaline water electrolysis was developed by Grubbs and subsequently advanced by General Electric Co. in 1966. PEM water electrolysis is very analogous to PEM fuel cell technology as they both deploy a sulfonated polymer membrane as the electrolyte. For PEM electrolysis, the proton or hydrogen molecule is the ion-conducting species. The electrochemical reactions can be facilitated by deionised water permeating through the proton-conductive membrane. Whereas AEM electrolysis uses a solid anion exchange membrane that contains quaternary ammonium functional groups to facilitate the ion-transfer of hydroxide ions (OH^-) between the cathode and anode, alkaline water electrolysis uses porous diaphragms (*e.g.*, asbestos) for the same purpose.[48] Thus, the solid membrane provides an effective separation of product gases which improves the safety and compactness of the system. Schematic representation of the AEM electrolysis process is shown in Fig. 6. Water is reduced at the cathode, forming hydrogen and hydroxide ions, whereas oxygen is produced at the anode. By using a solid polymer

Table 6 Representative bifunctional catalysts for alkaline water electrolysis in 1 M KOH medium

S. no	Catalyst	Over potential @10 mA cm^{-2} (HER/OER)	Cell voltage	Tafel slope	Stability	Key features	Ref.
1	MoS_2@$Ni_{0\cdot96}S$	104/182 mV	1.86 V	—	15 h	Strong MoS_2–NiS interface, abundant active sites	43
2	NiCo–Co_2O_4@Cu_2O@CF	133/327 mV	1.69 V	119/118	12 h	Excellent adhesion, nano-heterostructure	44
3	$NiCo(OH)_2$@CF	119/315 mV	1.94 V@1 A cm^{-2}	112/66	30 h	2D nanoflakes, rapid charge transfer	45
4	Ni–Mo–NiMo@NC	61 (HER only)	—	99	—	N-doped carbon shell, enhanced conductivity	46
5	Ni_2P/N@$Ti_3C_2T_x$@NF	15 (HER)	—	30	3000 cycles	Strong H* binding, 3D porous MXene support	47

membrane, the problems of electrolyte leakage and carbonation, which are common in alkaline water electrolysis systems, have been eliminated. In addition to the above, the solid membrane structure allows for smaller distances between the electrodes compared with liquid alkaline electrolysis systems.

One of the major benefits of the AEM water electrolysis technology (AEMWE) is its use of catalysts that do not require precious metals, such as nickel, cobalt, and iron. This creates a huge value because these transition metals are far less costly than the noble metals that are used in the proton exchange membrane (PEM) electrolysis technology (*e.g.*, platinum, iridium). Another advantage of the AEM system is the ability to operate with either high purity water or very low concentrations of alkaline electrolytes (*e.g.*, 0.5–1 M KOH in comparison to traditionally concentrated alkaline electrolytes of 5–7 M KOH). This reduces the possibility of corrosion, simplifies the system design, and increases the safety of operations. In recent years, a number of developments in the field of AEM technology have been directed towards increasing the conductivity, chemical stability, and mechanical strength of the membrane. In addition, a variety of advanced membrane materials with improved alkaline stability and degradation resistance are currently under investigation. Major advances in catalyst engineering have also taken place, including the development of nanostructured electrodes, bimetallic catalysts, and surface-modified materials that improve the rate of reaction for both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Despite the technical progress, there are still many obstacles to overcome before widespread commercialization can occur. Membrane degradation at high alkaline conditions and oxidative conditions continues to be a significant problem that can result in a decrease in the performance of the AEM. The stability of the membrane-electrode assembly (MEA) is also a critical issue that has an impact on the longevity of the MEA and its performance during long-term operations.

Another significant limitation is water management within the cell. To ensure stable operation, the membrane must remain optimally hydrated while avoiding flooding or drying out of the electrodes. Additionally, carbon dioxide from the atmosphere may react with hydroxide ions in the process of producing carbonate compounds that can reduce system efficiency and ionic conductivity as it ages. From a systems perspective, AEMWE has tremendous potential as a partner with renewable energy sources like wind and solar because of the relatively low cost and flexibility of operation. Furthermore, because AEMWE can use intermittent power, it has the potential to provide decentralized hydrogen production and energy storage opportunities. Researchers will continue to work on scaling up, developing improved stack designs and lowering total system costs to help maximize the $H21 P5 Target. In general, AEM water electrolysis is an exciting technology representing a potential bridge between traditional alkaline and PEM technologies. AEM water electrolysis incorporates low-cost, highly performing characteristics to create a well-balanced alternative technology. Ongoing advances in material science, cell design, and long-term durability research will

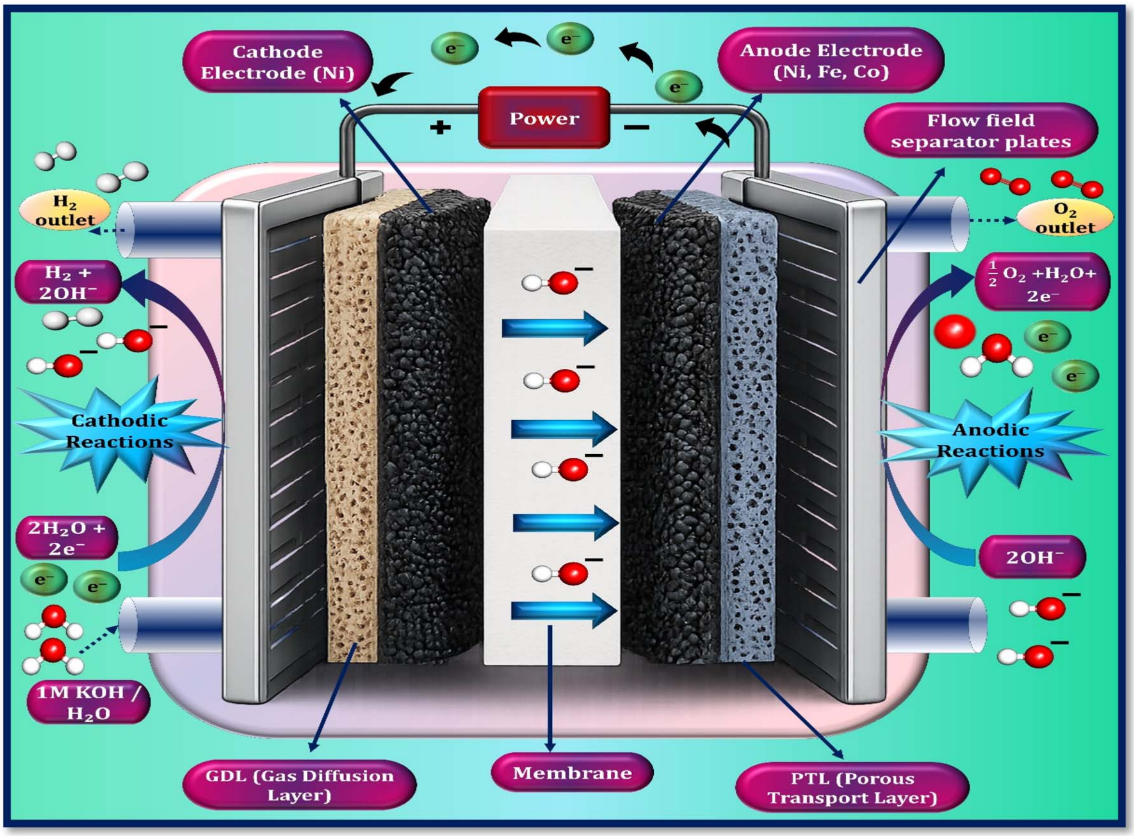

Fig. 6 Mechanistic illustration of anion exchange membrane water electrolysis with ion transport and electrode reactions.

Table 7 Summary of advanced non-noble electrocatalysts for anion exchange membrane (AEM) water electrolysis in alkaline media

S. no	Catalyst	Method	Electrolyte	Performance	Stability	Key point	Ref.
1	3D-a-NiFeOOH/N-CFP	Single-step electrodeposition	1 M KOH + AEM electrolyzer	η: 170 mV@10 mA cm^{-2}; Tafel: 39 mV dec^{-1}; cell: 1.88 V; Eff.: 80%	240 h; 95.6% retention	3D structure + Fe improves OER, better than IrO_2	49
2	Cu–Co–P_{1200}/CP	Co–P deposition + Cu addition	Alkaline + AEM electrolyzer	η: 59 mV@10 mA cm^{-2}; Tafel: 38 mV dec^{-1}; cell: 1.9 V	Stable in alkaline	Cu boosts activity; comparable to Pt/C–IrO_2	50

allow companies to compete with AEMWE in large-scale hydrogen production as shown in Table 7.

3.1.3 Proton exchange membrane (PEM) water electrolysis. Compared to alkaline systems, PEM water electrolysis has much quicker kinetics for producing hydrogen. This is mostly due to the highly active surfaces of the Platinum bar and the very acid of the operating environment. The acid aids with the rapid transport of hydrogen ions, and there is little activation loss allowing for the possibility of very high current levels, thus making possible a very high production of hydrogen. Also, because the electrolytic solution is in the form of a solid polymer membrane rather than a liquid alkaline solution, the operation is much safer, with significantly lower risk of leakage or spillage. Lastly, there are many advantages to the compact design, high power density and, the ability to use dynamic operation of the PEM electrolyzer, allowing for the integration of renewable energy from intermittent sources such as wind and solar.[51] Recent work performed on PEM electrocatalysts and their respective electrochemical performance evaluation is presented in Table 8.

PEM water electrolysis is achieved *via* electrochemical decomposition of water to produce hydrogen and oxygen (Fig. 7). Water molecules are oxidized at the anode to produce oxygen gas, protons (H^+) and electrons. The oxygen generated is released from the anode compartment; protons migrate through the proton exchange membrane to the cathode while electrons move *via* an external circuit to provide electrical current. At the cathode, the protons recombine with the

Table 8 Summary of recent advancements in PEM water electrolyser electrocatalysts and their electrochemical performance

S. no	Catalyst	Electrolyte	Key performance	Stability	Key point	Ref.
1	PtNW/Ti	PEM (acidic)	63 mV@100 mA cm^{-2}; 1.643 V	Stable, low Pt usage	High efficiency, low cost	52
2	MoS_2 NSs/CFP	0.5 M H_2SO_4	192 mV; 2.25 V	Better than Pt/C	Low cost, ionomer-free	53
3	Ti–MoP	0.5 M H_2SO_4	81.5 mV@10 mA cm^{-2}	8000 cycles, 15 days	Improved activity & stability	54
4	Co–$P_{0\cdot3}$	Acidic (H_2SO_4)	143.85 mV	Durable	PGM-free, scalable	55 and 56
5	NiMo@N–C	PEM	~2.2 V	10 000 cycles	Acid-stable, noble-metal-free	57
6	MoS_2@BPPC	Hydrothermal	0.5 M H_2SO_4	150 mV, 51 mV dec^{-1}	100 h stable	58
7	FeP/CB	Phosphidation	0.5 M H_2SO_4	252 mV	Stable	59
8	Ir@WO_3 NRs	Electrodeposition	PEM (acidic)	2.2 A cm^{-2}@2.0 V	1030 h	60
9	Ir–Ru@WO_3	Electrodeposition	PEM (80 °C)	245 mV	500 h	61
10	IrO_2/N–CN	Annealing + hydrothermal	PEM acidic	High activity	300 h	62
11	W–TiO_2 (IrO_2)	Co-precipitation	PEM	1 A cm^{-2}@1.602 V	Improved	63
12	Core–shell Ru@Ir nanostructure	Controlled core–shell synthesis with oxygen incorporation	Acidic medium – 0.5 M H_2SO_4 – acidic conditions	238 mV@10 mA cm^{-2} – Tafel slope: 92.6 mV dec^{-1} – mass activity: 78× higher than commercial IrO_2@1.55 V	Unsupported IrO_2 and commercial IrO_2	64
13	Core–shell IrGa–IrO_2 (IrGa intermetallic core, oxidized Ir shell)	Intermetallic synthesis + partial oxidation	Acidic electrolyte – PEM configuration	272 mV@10 mA cm^{-2}; Tafel slope: 57.2 mV dec^{-1}; mass activity: 84.1 A g^{-1}@1.52 V (3.6× Ir/C = 232 A g^{-1})	Ultra-low Ir loading (exact not stated) with robust performance	65

electrons to produce hydrogen gas. The proton exchange membrane selectively conducts protons while preventing the crossover of gases, ensuring the high purity of hydrogen produced by this process.

Recent advances in PEM electrolysis research have aimed to improve the efficiency of electrolysis catalysts, increase their life spans, and reduce their costs. The two most commonly used noble metals for electrolysis catalysis are platinum (Pt) and iridium (Ir) due to their higher levels of catalytic activity and stability when used in acidic conditions; however, their high price and limited availability continue to be a significant barrier to commercialization. As a result, a considerable amount of research is being conducted to reduce the amounts of noble metals required to create effective catalysts by developing alloy-based catalysts and finding alternative or non-noble metals that perform similarly to noble metals. The innovation of membrane materials has also helped to improve the efficiency of PEM systems; newer membrane materials have superior chemical stability and higher proton conductivities compared to traditional membranes, which should lead to improved overall system performance and longevity. The high current densities that PEM electrolysis systems can accommodate (usually more than 2 A cm^{-2}) allow for rapid hydrogen production within small physical footprints; therefore, PEM electrolysis technology can provide high-quality hydrogen fuel very quickly, providing an ideal source of hydrogen fuel for applications that rely on variable renewable energy (*e.g.* wind or solar). Nevertheless, several key challenges still need to be addressed before large-scale commercial implementation of PEM water electrolysis can happen: membrane degradation; catalyst dissolution; and system cost reduction. Meanwhile, continued innovations in materials science, system design, and manufacturing technologies will provide further improvements to the performance, durability, and commercial feasibility of PEM water electrolysis technologies.

3.1.4 Solid oxide electrolysis. SOECs are a type of high-temperature (HT) electrochemical device that uses electrical energy to produce hydrogen from steam, thus converting electrical energy into chemical energy. SOEC operates in the range of 500 to 850 degrees Celsius; it takes advantage of the use of thermal energy to drive the water-splitting reaction as a means to greatly reduce the amount of electrical energy needed to produce hydrogen compared with producing hydrogen from low-temperature electrolysis devices. Since electricity is typically the dominant cost component of producing hydrogen, reducing the amount of electrical energy required has a large impact on the economic viability of producing hydrogen from SOEC and decreasing the cost of producing hydrogen from SOEC. SOECs also operate at higher efficiency, have better thermodynamic and faster electrochemical kinetics (reaction rates) because of their elevated operating temperature resulting in lower over potentials and higher current densities than PEM and alkaline electrolysis devices; SOECs therefore have higher conversion efficiencies than either PEM or alkaline electrolysis devices. The use of steam instead of liquid water in SOEC also reduces the mass transfer limitations and results in improved reaction rates overall.

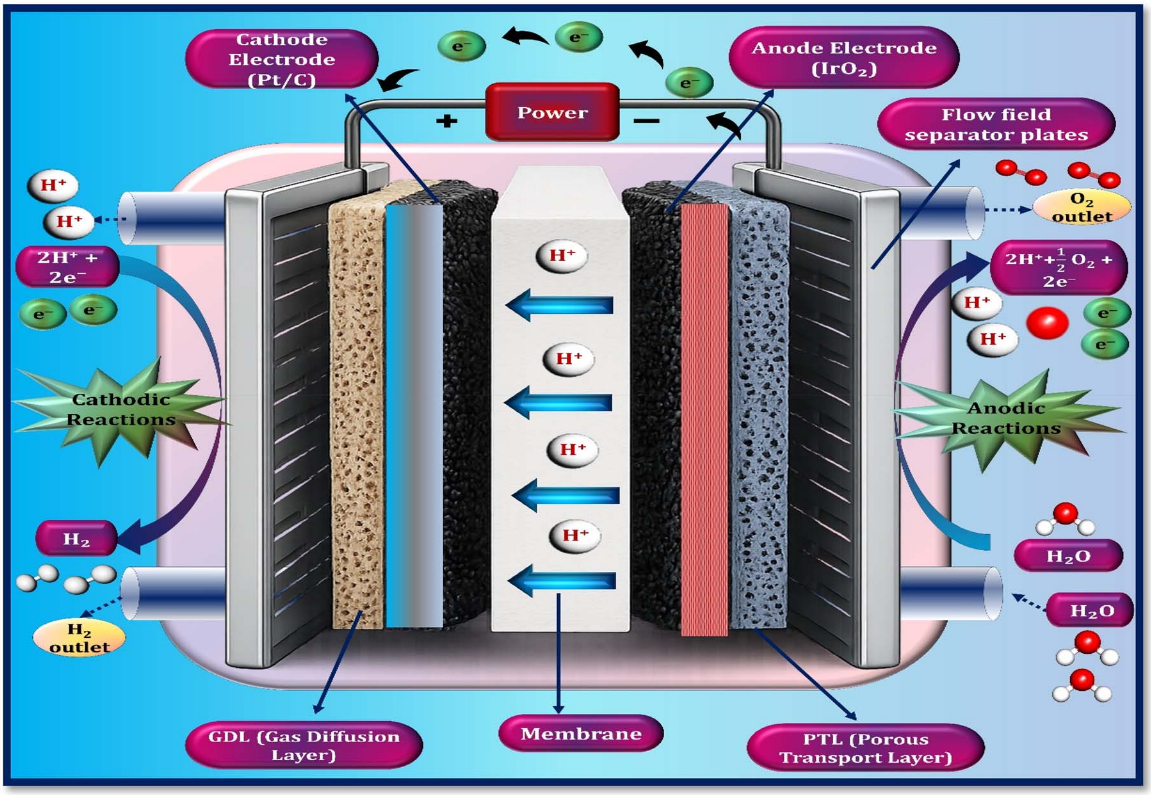

Fig. 7 Mechanistic schematic of proton exchange membrane water electrolysis highlighting proton transport and electrode reactions.

SOEC technology has key flexibility when it comes to system integration. It can easily be combined with both industrial waste heat sources and a number of other heat sources such as nuclear reactors and concentrated solar power systems; when this happens, improved energy utilization is the result. Additionally, SOECs can operate in co-electrolysis mode where both steam and carbon dioxide can be reduced at the same time to produce hydrogen and carbon monoxide (syngas), allowing for easy integration with downstream processes like Fischer–Tropsch synthesis and methanol production; therefore, it makes them very attractive for producing sustainable fuels and chemicals. However, some technical challenges continue to exist. One of these challenges is high operating temperature, which can cause material failures, thermal stress, long-term stability issues with electrolytes, electrodes and interconnects. Other issues include sealing problems and the need to withstand thermal cycling.[66] Engineering efforts have to be made in order to address these issues in terms of durability and scalability. Researchers are currently working to develop more robust electrode materials; improve the conductivity of the electrolytes and optimize cell architectures for performance and lifespan. Overall SOEC technology offers an exciting opportunity for greater efficiency and larger volume hydrogen production if combined effectively with renewable/waste heat sources. Table 9 summarizes some of the most recent advances in SOEC material, configuration, and performance, showing advancement toward commercial viability.

SOEC stands for solid oxide water electrolysis; a solid oxide water electrolysis (SOEC) system runs at a range of temperatures from approximately 500–850 °C, using steam as the feedstock for producing hydrogen gas and oxygen gas *via* an electrochemical reaction. As seen in Fig. 8, within SOECs, the initial reaction occurs at the cathode where steam molecules react with electrons to create hydrogen gas and oxide anions (O^{2-}) When hydrogen gas is formed at the cathodes it is released into the surrounding environment, while oxide anions that were formed at the cathodes will then flow through a dense ceramic electrolyte (typically a yttria-stabilized zirconium oxide) to reach the anodes. At the anodes, the oxide anions are oxidized by releasing electrons to create oxygen gas; and these electrons return back to the cathodes through an external electrical loop, enabling continuous operation of the cell.

SOEC (solid oxide electrolysis cell) has several advantages over standard electrolysis. Some are high-efficiency conversion from thermal energy to electrical energy, and thus lower overall electric consumption of SOEC compared to low-temp electrolysis technologies (alkaline and PEM) because some of the overall energy used for water splitting comes from heat. This makes SOEC systems ideal for integration with high-temperature heat sources (nuclear, CSP, and industrial waste heat streams). SOEC reaction kinetics are enhanced at elevated temperatures resulting in lower activation losses (higher current densities). The use of solid-state components in SOEC eliminates problems associated with liquid electrolytes, including corrosion and electrolyte management issues.

Table 9 Recent developments in solid oxide water electrolysis technology and their electrochemical performances

S. no	Electrode	Description	Electrolyte	Operating temperature (°C)	Current density/velocity	Stability/performance	Ref.
1	R-NiCdO–SDC composite electrode	Hydrogen electrode for reversible solid oxide cells with enhanced electron vacancies	Reversible solid oxide cell	700	265 mA cm^{-2} at 1.4 V	Stable for 10 h under 47% H_2O–53% H_2 atmosphere	67
2	$BaNdFeO_3$ perovskite (Co-free)	Oxygen electrode with high electronic conductivity (24.3 S cm^{-1}) and low TEC (18.5 × 10^{-6})	Solid oxide cell	800	2.05 A cm^{-2}	Lowest polarization resistance among YSZ symmetric cells	68
3	Mn-doped $LaSrNiO_4$ (LSNM)	Ruddlesden–Popper oxide oxygen electrode	Solid oxide electrolyzer	800	500 mA cm^{-2} at 1.4 V	0.488 Ω cm^2 resistance; stable for 145 h; 85.2% higher than un-doped LSN	69
4	Ln_2NiO_4 (Ln = La, pr, Nd); Co-substituted $Pr_2Ni_{1-x}Co_xO_4$	Layered perovskite-based nickelates; Co substitution improved durability	High-temperature SOEC	800–900	3.0 A cm^{-2} (900 °C), 1.9 A cm^{-2} (800 °C) at 1.5 V	Degradation reduced to 22 mV kh^{-1} after 250 h at −1 A cm^{-2}	70

However, high operating temperatures present challenges including material degradation, thermal stress, sealing issues, and concerns regarding long-term stability. Common electrode materials include nickel-based cermets for the cathode, and perovskite-type oxides for the anode.

Another benefit of SOEC technology is its operational flexibility, with capability to operate in electrolysis mode and rSOC (reversible fuel cell) mode. In addition, it supports the co-electrolysis of steam plus CO_2 into syngas (hydrogen plus CO), a useful intermediate for synthetic fuels and chemicals. There is much work being done on completing the development of SOECs for commercialization; most barriers to commercialization are related to durability and cost of materials. Current research efforts will continue to improve electrode durability and reduce rates of degradation through improved materials and innovative systems for long term operation at minimum cost.

3.1.5 Direct seawater electrolysis. Hydrogen can be generated sustainably through the processes of both electrochemical (EC) and photochemical (PC) water splitting, but both methods depend strongly on access to clean, high-quality freshwater. With rapid population growth, industrialization, and increased scarcity of water resulting from climate change, reliance upon purified water is a significant barrier to the further deployment of green hydrogen technologies.[71] Seawater currently covers over 70% of Earth's surface, making it a plentiful and cost-effective alternative feedstock for hydrogen generation.

Seawater electrolysis generates hydrogen at the cathode through the hydrogen evolution reaction (HER). The competing reactions occurring at the anode during seawater electrolysis are oxygen evolution (OER), chlorine evolution (CER), and hypochlorite formation. Chloride ions present in the seawater create added challenges because they can also be preferentially oxidized instead of water, which leads to side reactions that yield chlorine. Despite the extensive research that has been conducted on seawater splitting, production at scale still has a number of technical issues.

The slow rates of electrochemistry (the slow kinetics) for the OER (overall electrode reaction) are challenging and essentially require large amounts of energy (large over potentials) to operate efficiently. Chlorine is produced through a competing reaction at much lower over potentials than the OER; because of this, there will be a large reduction in the selectivity for the production of oxygen and system components will suffer corrosion from chlorine. These issues will ultimately lead to decreased energy efficiency, decreased catalyst lifetime, and increased operating costs. Seawater contains a number of impurities such as magnesium, calcium and organic matter, which can also lead to electrode fouling, precipitation/scale formation or membrane degradation after long-term operation. Recent work has been directed towards developing improved electrocatalysts and system designs that can both selectively promote the OER while suppressing the chlorine-producing reactions as is current practice. Some strategies include catalyst surface engineering, using corrosion-resistant materials, and utilizing protective coatings to improve the durability of components in a saline environment. Many

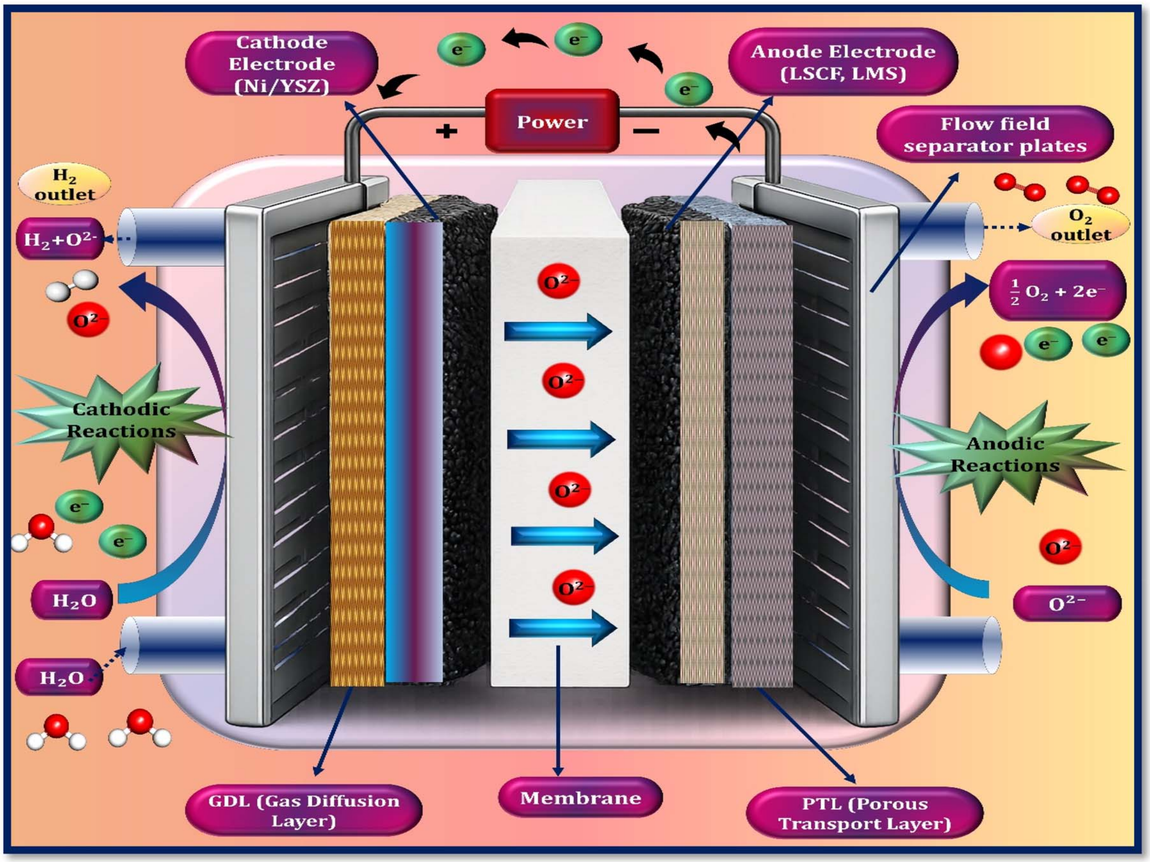

Fig. 8 Functional diagram of solid oxide electrolysis cell illustrating oxygen evolution and hydrogen production pathways.

transition metal-based catalysts, such as nickel-iron layered double hydroxides (NiFe-LDH), cobalt-based oxides and perovskite materials, have been demonstrated to have excellent activity and stability when used in alkaline seawater applications.[72]

A different approach is changing the conditions of the electrolyte. Alkaline medium can often be advantageous as they reduce the likelihood of chlorine being generated and therefore improve the selectivity towards OER. Pre-treating seawater or the use of hybrid systems that combine desalination with electrolysis can be an alternative that addresses impurities. However, such solutions may also introduce more complexity and cost to the system which demonstrates that optimized, integrated designs are necessary. Research is also focused on reducing the over potential of the OER below 0.48 V in alkaline seawater electrolysers, which is viewed as an important performance development target for improving the overall efficiency of the system. In addition to developing new catalysts, advancements in electrode design, membrane materials and reactor design are important contributors to improving seawater electrolysis performance and scalability. The eventual successful commercialization of seawater electrolysis will depend on achieving a good balance of efficiency, durability, and economic viability in seawater electrolysers. Continued research and innovation in materials science combined with the optimization of the entire system and the integration of renewable energy into seawater electrolysers is critical to fully realise the potential of seawater as a viable source for the production of green hydrogen. A thorough comparison of the technical parameters and performance metrics of various water electrolysis elecrolyser technologies is provided in Table 10.

3.2 Thermochemical pathways

3.2.1 Supercritical water gasification. Supercritical water gasification (SCWG) is a cutting-edge process of producing hydrogen that makes use of rather extreme conditions of pressure and temperature, allowing water to become both a very high-temperature and very-high-pressure medium for performing chemical reactions with biomass materials. The high temperature and high pressure that make up the conditions for SCWG result in water also having the ability to provide exceptional solvation properties, meaning that it can break down "wet" organic feedstock materials into a hydrogen-rich gas product without having to first dry those materials. The supercritical state of water exists at pressures above 22.12 MPa and temperature above 372.12 °C. Within this super at supercritical state, water does not exhibit the characteristics of either a standard liquid or gas. The high temperatures (usually above 600 °C), enable the water to promote rapid decomposition or breakdown of organic feedstocks through a variety of chemical

Table 10 Technical characteristics of typical water electrolysis technologies.[73]

S. no	Parameter	Alkaline	AEM	PEM	Solid oxide
1	Anode reaction	$2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^-$	$2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^-$	$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$	$O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$
2	Cathode reaction	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$2H^+ + 2e^- \rightarrow H_2$	$H_2O + 2e^- \rightarrow H_2 + O^{2-}$
3	Overall cell	$H_2O \rightarrow H_2 + \frac{1}{2}O_2$	$H_2O \rightarrow H_2 + \frac{1}{2}O_2$	$2H_2O \rightarrow 2H_2 + O_2$	$H_2O \rightarrow H_2 + \frac{1}{2}O_2$
4	Electrolyte	KOH/NaOH (5M)	Divinylbenzene polymer with 1M KOH/NaOH	Solid polymer electrolyte (PFSA)	Yttria stabilized Zirconia (YSZ)
5	Electrode catalyst (H_2 side)	Nickel coated perforated stainless steel	Nickel	Iridium oxide	Ni/YSZ
6	Electrode catalyst (O_2 side)	Nickel coated perforated stainless steel	Nickel or NiFeCo alloys	Platinum carbon	Perovskites (LSCF, LSM, (La,Sr,Co,Fe), (La,Sr,Mn))
7	Gas diffusion layer	Nickel mesh	Nickel foam/carbon cloth	Titanium mesh/carbon cloth	Nickel mesh/foam
8	Bipolar plates	Stainless steel/Nickel coated stainless steel	Stainless steel/nickel coated stainless steel	Platinum/gold coated titanium or titanium	Cobalt coated stainless steel
9	Nominal current density	0.2–0.8 A cm^{-2}	0.2–2 A cm^{-2}	1–2 A cm^{-2}	0.3–1 A cm^{-2}
10	Voltage range (operating)	1.4–3 V	1.4–2.0 V	1.4–2.3 V	1.0–1.5 V
11	Operating temperature	70–90 °C	40–60 °C	50–80 °C	700–850 °C
12	Efficiency	50–78%	57–59%	50–83%	89% (laboratory)

reactions, including hydrolysis, pyrolysis, and reforming. These reactions produce hydrogen, carbon dioxide, methane and smaller amounts of carbon monoxide.

High moisture biomass (such as sewage sludge, agricultural residues, food waste, and algae) can be processed with supercritical water gasification without the need for any drying, making it an effective alternative to conventional thermochemical processes that have difficulty processing this type of biomaterial. The elimination of a drying step reduces both the total energy required for processing and increases the overall efficiency of the process. In addition, the supercritical state of water minimizes the production of tar and carbonized material (char) that are typically associated with conventional gasification methods. Catalysts are often used in SCWG systems to increase the amount of hydrogen produced, as well as to speed up the rate of reaction between water and biomass materials. Many transition metals (nickel, ruthenium, platinum) are popular choices for use as catalysts because they promote reforming reactions while reducing the formation of undesired by-products such as methane. The design of the reactor also plays a key role in SCWG process success because it must be constructed from materials that can withstand high temperatures, high pressures, and corrosive conditions.

SCWG has many advantages but there are many challenges to commercialising at larger scales including: high capital cost, degrading reactor materials, salt precipitation/clogging, and difficulty in operating continuously. Research is currently being done to improve the stability of catalysts used in this process, develop corrosion-resistant reactor materials, and optimise the process conditions so that hydrogen selectivity and economic viability are increased. Overall, SCWG is a very viable option for producing sustainable hydrogen, especially from wet biomass resources and waste biomass resources, therefore contributing to the circular economy while reducing environmental impacts.[74]

Pre-processing steps often improve waste-to-gas conversion system performance significantly and a critical process is the adjustment of moisture levels to a continuous range since too much water will reduce thermal efficiency; therefore, feedstocks must be processed to approximately 10–20% moisture. The material is also processed to have uniformity in composition and particle size to provide uniform reaction conditions in the reactor. Regardless of the method for gasification used, the path of conversion through several common phases occurs prior to syngas creation, as shown in Fig. 9.[75]

The removal of contaminants from the waste stream occurs first and is then blended to create a feedstock with uniform composition. The feedstock is then thermally dried with heat applied to a temperature of either 100 °C or higher, up to and including 200 °C to reduce moisture levels below 5%. Next, the feedstock undergoes thermal degradation in the same temperature range, where the complex organic compounds in the feedstock convert into basic products such as gas, char, or tar.

3.2.2 Thermochemical and industrial by-product hydrogen production. Thermochemical water-splitting cycles are seen as a very efficient and environmentally friendly way to create hydrogen using nuclear energy. The high-temperature heat

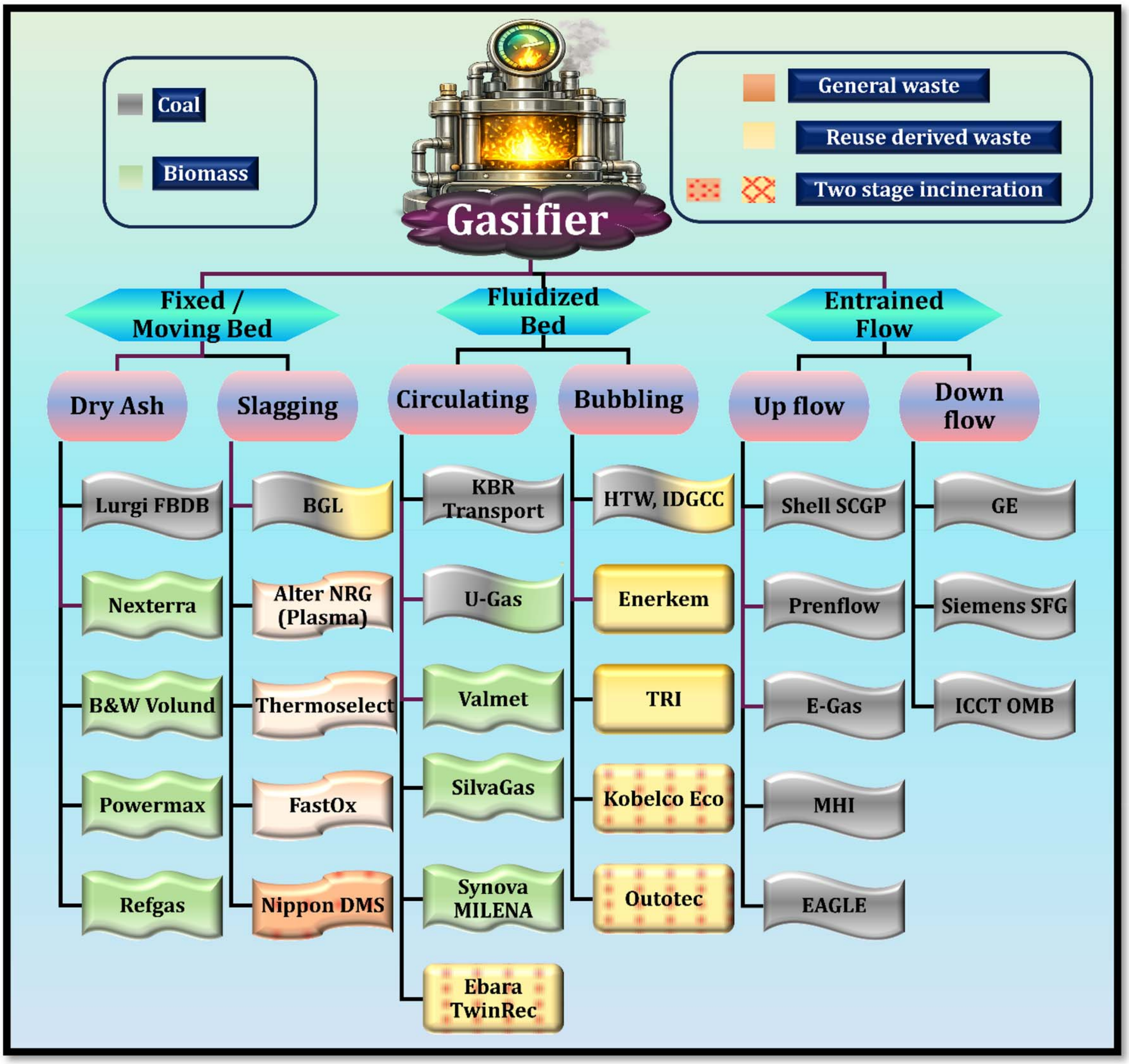

Fig. 9 Categorization of gasification technologies based on feedstock type and commercial deployment, reprinted from ref. 75 © Johnson Matthey 2023 under the Creative Commons Attribution 4.0 International License (CC BY 4.0).

produced in advanced nuclear reactors, like very high temperature reactors (VHTRs), can be used to produce hydrogen from water through a succession of endothermic and exothermic chemical reactions. Unlike traditional electrolysis, using this method uses very little electrical energy, allowing for greater overall energy efficiency and lower operating costs. Another major benefit of thermochemical cycles is that they are closed-loop systems. The chemical intermediates generated during the first part of the process are then recycled and reused during the second half of the process. Because of this, the amount of waste produced by thermochemical cycles is very minimal and only water is consumed during the entire process. As such, thermochemical cycles are very environmentally friendly and create only hydrogen and oxygen as product outputs, producing no greenhouse gases directly from the process. There have been many different thermochemical cycles developed and analysed, including the copper-chlorine (Cu–Cl) cycle, hybrid sulphur cycles, and metal-oxide based cycles. Of these, the sulphur-iodine (SI) cycle is the most developed and has been suggested as one of the most promising technologies for large-scale hydrogen production due to its high theoretical efficiency and the ability to use high temperature thermal energy to generate hydrogen.

One of the major advantages of thermochemical and high-temperature hydrogen production pathways is that elevated operating temperatures reduce the thermodynamic energy required for water decomposition compared with conventional low-temperature electrolysis. Consequently, these approaches have attracted considerable interest for integration with advanced nuclear reactors, concentrated solar thermal systems, and industrial waste-heat recovery processes. In comparison with conventional electrolysis, thermochemical cycles may offer improved overall system efficiency by minimizing electrical energy consumption while utilizing thermal energy more effectively.[76]

The Bunsen reaction, sulfuric acid decomposition, and hydrogen iodide decomposition are the three major reaction steps that make up the SI cycle. In the first step, hydrogen iodide (HI) and sulfuric acid (H_2SO_4) form when iodine (I_2), sulfur dioxide (SO_2), and water react together. The resulting products, hydrogen iodide and sulfuric acid, then separate into two different streams. Subsequently, sulfuric acid thermally decomposes at high temperatures, creating SO_2, oxygen (O_2), and water, thereby creating more SO_2 to recycle into the first reaction stream. Concurrently, hydrogen iodide also decomposes to produce hydrogen gas (H_2) and iodine (I_2) with the iodine recycled back into the initial reaction. The SI cycle's major challenge is to operate at very high temperatures, typically between 800–900 °C, using highly corrosive chemicals such as sulfuric acid and iodine. Therefore, research on the development of new materials with greater thermal stability and corrosion resistance is critical for succeeding in this application. Efficient separation and purification of all intermediate products is also key to maintaining the performance efficiency of the SI cycle; therefore, research and development activities continue to improve catalyst performance, heat integration, and system design.[77] The typical configuration of the SI Cycle is shown in Fig. 10, which depicts the connection between the three reaction steps and the continual recycling of chemical species involved in the three reaction steps of the SI Cycle.

Cycles that use heat to break water into hydrogen and oxygen are known as thermochemical cycles. They consist of several chemical reactions which produce intermediate products, and all of the intermediate products are returned to the reaction to produce only hydrogen and oxygen. Without relying primarily on direct electrical energy input, thermochemical cycles utilize high-temperature thermal energy to drive water-splitting reactions. Since thermochemical cycles use little to no catalysts, the primary reactant in the system is water, while all other components of the cycle are recycled. Thermochemical cycles operate at extremely high temperatures by using large amounts or massive quantities of heat energy developed by a variety of advanced or high-temperature heat sources, including advanced nuclear reactors, concentrated solar power, and industrial process heat. Thermochemical cycles can be classified based on the number of reactions involved, which can include two-step, three-step, and multistep cycles. Each of these thermostable cycles can have different levels of efficiency, material use, and complexity. Thermochemical cycles that have been studied for many years and have good potential to produce large amounts of hydrogen include the S–I cycle, Cu–Cl cycle and HyS cycle.

Thermochemical cycles provide numerous benefits due to their potentially higher thermal efficiency and reduced electrical energy demand compared with conventional low-temperature electrolysis. The fact that thermochemical cycles do not have intermediate energy conversion losses helps make them highly efficient. Advanced recycling of chemical

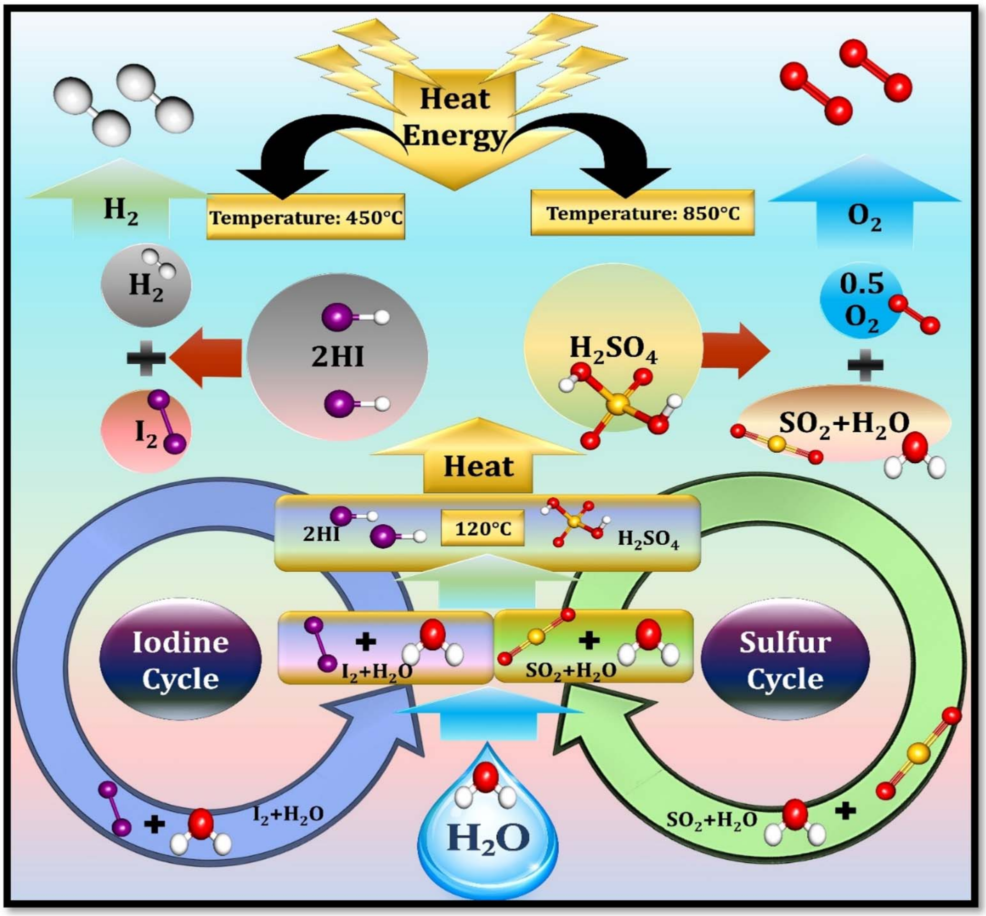

Fig. 10 Schematic flow diagram of the standard SI cycle for hydrogen production.

intermediates decreases the amount of primary materials consumed and also greatly reduces any environmental harm. However, several challenges exist for the practical application of the thermochemical cycle, including the damage to materials from high temperatures, corrosion of materials from the action of the reactive intermediates, and the need for efficient processes for heat integration and separation. Nomenclature of returnable materials and sustainable technology improvements will advance the development of durable materials that can withstand high temperatures, in high-stress operating environments. As technology continues to develop, thermochemical water-splitting cycles will be significant contributors to the supply of large amounts of hydrogen with minimal impact on the environment while being generated by renewable and nuclear energy sources.[78]

In addition to dedicated thermochemical hydrogen production systems, substantial quantities of hydrogen are generated as industrial by-products in chlor-alkali plants, ammonia manufacturing, chlorate and perchlorate production, petroleum refining, coagulant manufacturing, and heavy-water processing associated with nuclear technologies. In many industrial facilities, a portion of this hydrogen remains underutilized, flared, or vented instead of being recovered for energy applications. Therefore, improved hydrogen recovery, purification, and utilization strategies may provide an economically attractive transitional pathway for expanding hydrogen availability while simultaneously reducing industrial emissions and improving overall resource efficiency.[79]

As shown in Fig. 11 two types of thermochemical water-splitting processes exist: pure thermochemical cycles use thermal energy to drive the reactions (thermochemical cycles), while hybrid cycles use both thermal energy and some other form of energy as part of the thermochemical reaction scheme (hybrid cycles). In these two types of processes, water will ultimately be split into hydrogen and oxygen using heat sources at high temperatures: typically, *via* concentrated solar or nuclear reactors with either electrical or photonic energy as auxiliary sources. When decomposing the water into hydrogen and oxygen, there are several intermediate steps that can be performed at lower temperatures (typically below 2000 degrees Celsius) than if this were accomplished in a single, high-temperature reaction, resulting in better thermodynamic performance. In addition to being more thermodynamically efficient, these processes also improve the economic viability of the process due to more frequent recycling of intermediate reactants.

Among industrial by-product sources, the chlor-alkali industry is currently one of the largest established producers of high-purity hydrogen suitable for downstream energy applications.

3.2.3 Microbial electrolysis and photo-fermentation. MECs can be defined as a type of advanced bioelectrochemical system that produces hydrogen gas (H_2) from organic materials contained in waste water. In this system, electroactive (electrogenic) microbes in the anode will oxidize (decompose) organic materials, and release electrons, protons, and carbon dioxide. If a small amount of outside voltage (greater than 2 volts), is supplied, those electrons and protons will be driven toward the cathode and combine to form hydrogen gas.[80,81] MEC systems are normally classified by two main configurations; single chamber configurations *vs.* dual chamber configurations, which are determined by their physical construction characteristics. A comparison of single *versus* dual chamber configurations is provided in Table 11. In single chamber MECs, the oxidation of organic materials occurs in the anode and hydrogen production occurs at the cathode inside a single chamber. This causes the potential for the production of unwanted gases including carbon dioxide (CO_2), methane (CH_4), and hydrogen sulfide

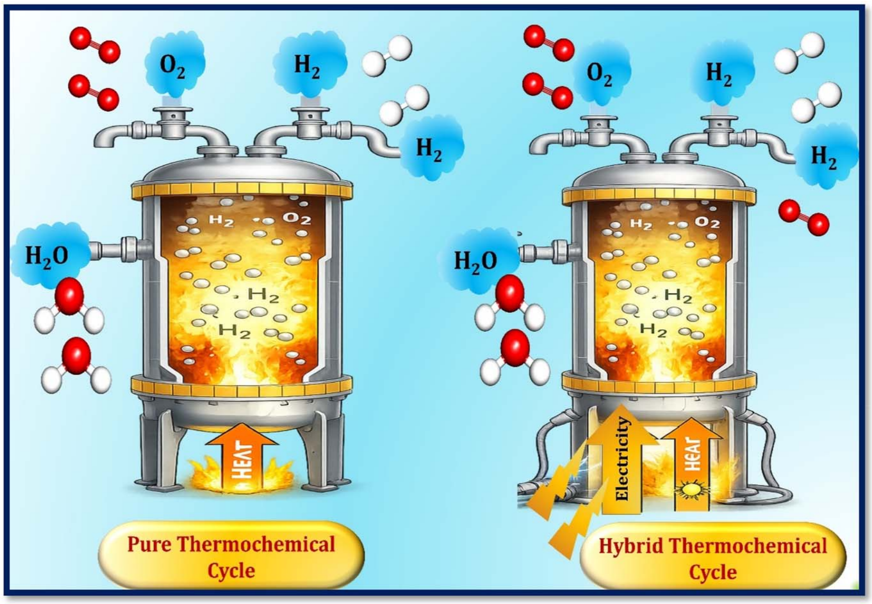

Fig. 11 Generalized diagram of pure and hybrid thermochemical pathways.

(H_2S). These unwanted gases are created by cross-contamination due to the mixture of numerous microbes in the anodic biofilm; including methanogens and sulfate reducing bacteria, as well as electrogenic species. Methanogens consume hydrogen and carbon dioxide to produce methane, so the hydrogen produced is reduced as a result. Methanogenesis is the major constraint on the hydrogen.[82,83]

Biological fermentation is an appealing method for achieving two goals simultaneously: treating wastewater, and producing hydrogen as an energy source. Both wastewater treatment H^+ production can support the circular economy and be used within "circular bioeconomy" applications. There are two modes of biological fermentation which are dark fermentation and photo-fermentation that can either be performed separately or together to increase both the hydrogen recovery rate and efficiency in utilizing the substrates. The anaerobic bioconversion process of dark fermentation is done using facultative anaerobes (such as *Enterobacter* woefully) and obligate anaerobes (usually *Clostridium* spp.) that convert many types of organic materials into one or more of the following products: hydrogen, carbon dioxide, and various volatile fatty acids (acetic acid, propionic acid, butyric acid, *etc.*). Acceptable feedstocks may include carbohydrate-rich industrial waste streams, food-processing wastes, lignocellulosic biomass (wood and agricultural residue), sewage sludge, and municipal solid waste (MSW) (42). In the acidogenic phase, complex organic molecules are broken down through hydrolysis (a decomposition reaction that utilizes the presence of water) and converted into hydrogen, carbon dioxide, and soluble metabolites such as volatile fatty acids (*i.e.*, acetic acid, propionic acid, butyric acid, *etc.*) *via* fermentation reactions.[95] Dark fermentation is quick, operates in the absence of light/photons, and has the capability of handling large loads of organics; however, the limits placed on dark fermentation's hydrogen production capabilities are due to the formation of reduced by-products.

Photosynthetic bacteria, such as purple non-sulphur bacteria (like *Rhodobacter* or *Rhodopseudomonas*), purple-sulphur bacteria, and green-sulphur bacteria, perform photo-fermentation. They are photosynthetic organisms that utilize light energy to convert organic acids (mainly those produced during dark fermentation) into hydrogen *via* nitrogenase pathways. The process occurs under anaerobic or micro-aerophilic conditions, requiring controlled light intensity, temperature and pH. Photo-fermentation may provide a greater yield of hydrogen, but is generally slower and more sensitive to operating conditions than dark fermentation.[96]

The quality of the overall hydrogen production is also directly affected by certain operational parameters for both processes. The primary operational parameters that impact process efficiency include pH, temp., hydraulic retention time (HRT), substrate concentration, and composition of the microbial community growing in the reactors that are being used. For example, dark fermentation can achieve maximum efficiencies when operating at pH 5.0–6.5 within a temperature range of 30–40 °C (mesophilic) or 50–60 °C (thermophilic), while photofermentation will require the reactor's pH to be close to neutral (pH 6.0–8.0) and provide constantly lighted environments. Reactor configurations vary when optimizing process performance; the basic types include continuous stirred tank reactors (CSTR), packed bed reactors, and photobioreactors.

4 Water pretreatment and conditioning techniques

Conditioning and pre-treatment of water are key components for efficient operation of systems that treat water for reuse and hydrogen production, as they affect greatly the effectiveness and durability of electrochemical and catalytic reactors. The goal of the preliminary processing is to remove suspended particles,

Table 11 Comparison between single- and dual-chamber microbial electrolysis cells (MECs)

S. no	Parameter	SCMEC (single-chamber)	DCMEC (dual-chamber)	Ref.
1	Structure	Single reactor without membrane	Two chambers separated by membrane	84
2	Working	Bacteria break organic matter; electrons go directly to cathode to produce H_2	Similar process, but ions pass through membrane to keep gases separate	85
3	Design	Simple, compact, low cost	Complex, needs membrane setup	86 and 87
4	H_2 production	Moderate efficiency; examples show good yield with low voltage (0.6–0.8 V)	Higher and more stable yield; advanced methods improve performance	88
5	Internal resistance	Low (electrodes are close)	High (due to membrane and spacing)	89 and 90
6	Voltage need	Low (≈0.2–1.0 V)	Slightly higher voltage required	91 and 92
7	Advantages	Low cost, easy maintenance, suitable for wastewater	High hydrogen purity, stable operation	93
8	Challenges	Methane formation, gas mixing, biofouling	High cost, voltage loss, pH imbalance, complex maintenance	94

colloids, salts, and other contaminants that may cause problems, such as fouling or scaling, when using electrochemical methods. Choosing a method is determined by the features of the initial water supply, quality requirements, and the end purpose of the water treatment. As shown in Fig. 12, traditional pre-treatment comprises a series of processes aimed at gradually improving the quality of water. There are several pre-treatment options, including filtration, coagulation–flocculation, ion exchange, and membrane technologies, which may be used separately or in combined setups.[97]

Other than the aforementioned processes, more complex pre-treatment processes are commonly applied to fulfill the demanding water quality needs of contemporary hydrogen production plants. For example, the use of advanced oxidation processes (AOPs) like ozonation, ultraviolet/H_2O_2 process, and photocatalysis is very effective in breaking down persistent organic compounds and emerging contaminants. Biological processes such as aerobic and anaerobic methods are also highly efficient in reducing the organic content of the influent before proceeding to additional pre-treatment stages. In addition to the mentioned processes, ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) processes play an integral role in producing extremely pure water to be used in PEM and alkaline electrolyzers. Through this treatment method, impurities like ions, organisms, and other pollutants are effectively removed from the influent water, resulting in higher water purity. Nonetheless, membrane fouling remains a key issue, hence the need for pre-treatment.

Moreover, pH adjustment, softening, and dechlorination are often necessary conditioning steps to prevent scaling, catalyst poisoning, and corrosion of system components. For example, hardness removal minimizes the deposition of calcium and magnesium salts, while dechlorination protects sensitive membrane materials and catalysts from oxidative damage. In integrated wastewater-to-hydrogen systems, real-time monitoring and control of water quality parameters such as turbidity, total dissolved solids (TDS), chemical oxygen demand (COD), and conductivity are essential to maintain stable and efficient operation. Overall, a well-designed pre-treatment and conditioning framework not only enhances hydrogen production efficiency but also reduces maintenance costs, extends equipment lifespan, and ensures compliance with environmental and operational standards.

Birthing hydrogen with the fermentation process is advantageous, however several challenges have to be solved to achieve success: produce low hydrogen amounts; work out an appropriate way to make them stable; not be able to see through the medium (*i.e.* light penetrating into it) (with the exception of how light can be used for photofermentation); and have a good way to get the gas out of the reaction vessel. Research is currently being conducted in these areas using genetic engineering to alter microbial strains or optimise the processes used in the production of hydrogen using fermentation; designing hybrid reactors; and coupling fermentation with other technologies (such as microbial electrolysis cells) to be used on a larger scale. Obviously, if successfully integrated fermentation systems can

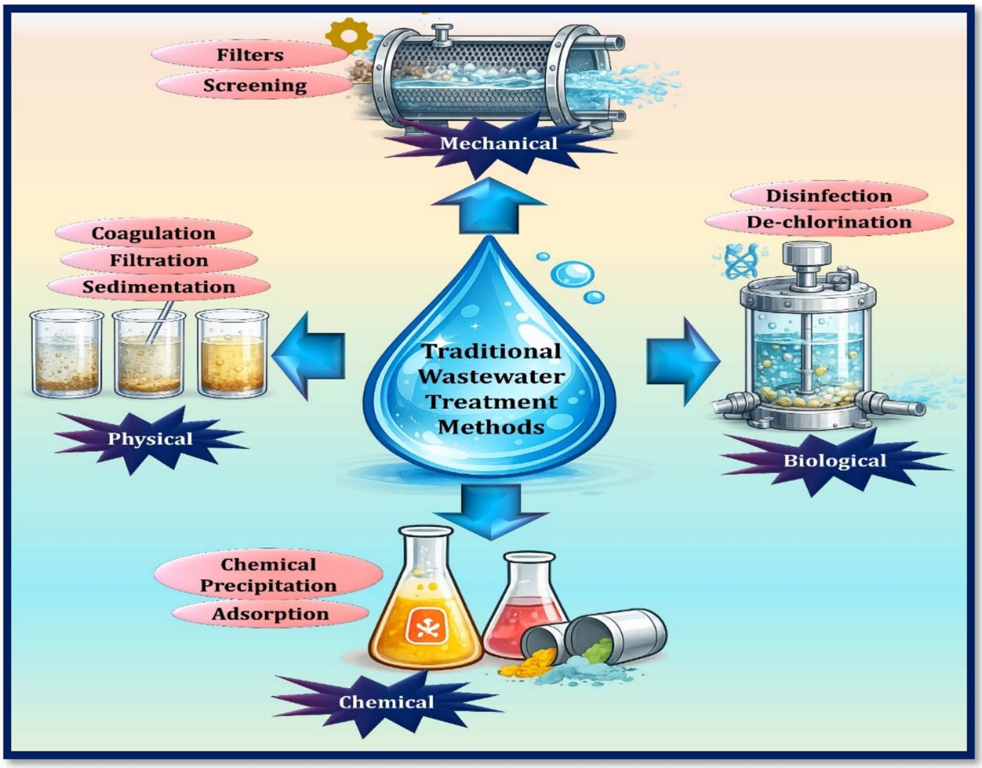

Fig. 12 Overview of conventional wastewater treatment techniques.

Table 12 Comparative summary of physical and chemical pretreatment methods for wastewater treatment

S. no	Method	Mechanism	Primary role	Typical target contaminants	Advantages	Challenges	Ref.
1	Coagulation/ flocculation	Chemicals (such as alum or ferric salts) are used to clump small particles into bigger flocs, which settle or can be filtered	Eliminate suspended solids and turbidity	Suspended solids, colloids, some metals	Simple, low cost, improves clarity	Produces sludge; depends on pH and dosage	101
2	Filtration	Water passes through media (sand, cloth, or membranes) to trap particles	Reduce solids and protect downstream units	Suspended solids, bacteria, organics	Easy operation, scalable	Needs periodic cleaning, less effective for dissolved compounds	102
3	Screening/ sedimentation	Physical separation by screens or settling under gravity	Eliminate significant waste and dense solids	Grit, debris, coarse organics	Low cost, simple design	Ineffective for small particles and needs space	103
4	Ion-exchange	Pollutant ions are swapped with harmless ions on a resin surface	Remove dissolved ions and metals	Hardness (Ca^{2+}, Mg^{2+}), heavy metals	High selectivity, Reusable resins	Resin saturation and chemical application for regeneration	104
5	Membrane filtration	Pressure or electric force pushes water through selective membranes	Remove salts, small organics, and microbes	Dissolved salts, microorganisms, organics	Production of high-purity water, compact	High cost	105
6	Adsorption	Pollutants stick to surfaces like activated carbon or biochar	Remove dyes, odor, trace organics	Dyes, organics, residual COD	Effective for low-concentration pollutants	Adsorbent replacement/ regeneration needed	106

be developed, organic waste can be converted into clean hydrogen fuel while minimizing the environmental pollution caused by wastewater generation.

4.1 Physical and chemical pre-treatment

The first step in wastewater treatment is physical treatment, which focuses on removing large pieces of solid material, grit, suspended material and material that floats from the influent stream. Screening, grit removal, sedimentation, flotation and filtration are some common unit operations. These methods are important not just for decreasing the total pollutant load, but also for preventing operational problems (clogging, abrasion and fouling) in downstream units. Wastewater from industrial sources, particularly from textiles, dyeing and chemical manufacturing, is usually darkly coloured and has a high level of BOD (biological oxygen demand) and COD (chemical oxygen demand), as well as increased salinity and alkaline pH. Advanced physical methods, such as membrane filtration (microfiltration or ultrafiltration), DAF (dissolved air flotation) and centrifugation, are being used to improve the efficiency of solid–liquid separation. Equalization tanks are typically used to achieve a homogeneous flow and pollutant concentration, which helps to stabilize all future stages of treatment. The selection of physical treatment methods will depend on factors, such as the size distribution of the particles, the composition of the wastewater, the rate flow of the wastewater and economic factors capital cost and operating cost.[98]

Chemical treatment of pollutants is vital to improving the overall effectiveness of physical methods. Without chemical treatment, there are numerous dissolved and colloidal pollutants that mechanical processes alone cannot remove. Chemical treatment utilizes chemical agents to induce a chemical reaction such as coagulation–flocculation, neutralization, oxidation–reduction, ion exchange, and disinfection. Coagulating and flocculating media are commonly utilized to destabilize colloidal particles and promote aggregation of these colloidal particles into larger flocs, making it possible to remove them *via* sedimentation or filtration. Neutralization is important for adjusting the pH of water or wastewater to meet a designated acceptable level; this is particularly important for highly acidic or alkaline waste streams. Advanced oxidation processes (*i.e.*, ozonation, Fenton reaction, photocatalysis) are being used more frequently to achieve degradation of refractory organic compounds and to remove colour from the wastewater stream. Chemical precipitation is an effective method for the removal of heavy metals (*i.e.*, lead, chromium, and cadmium) by converting heavy metals into their insoluble forms. Disinfection with chlorine, ozone, or ultraviolet light is utilized to eliminate pathogenic microorganisms from being discharged or reused in receiving streams.[99] Chemical treatment has several advantages for treating industrial effluent; for example, chemical treatment can be particularly effective against persistent organic pollutants, synthetic dyes, solvents, surfactants, and other toxic inorganic species that are resistant to biological treatment methods. However, chemical treatments also have limitations, such as generating chemical sludge; increasing operating costs due to the consumption of chemical reagents; and requiring careful handling and storage of chemicals. Because of these limitations, chemical treatment is often combined with physical treatments or biological treatments to improve the efficiency and sustainability of the overall process. To meet increasingly stringent discharge standards and promote the reuse of water for agricultural and industrial purposes, modern wastewater treatment systems often employ hybrid treatment methods that utilize both physicochemical and biological processes. In wastewater treatment the physical and chemical processes used for treating wastewater work together to achieve complementary objectives: physical treatments create an initial clarification of the wastewater by removing large particles before chemical treatments are applied to completely remove the dissolved or hazardous contaminants still present in the wastewater.[100] Together these processes improve the efficiency of wastewater treatment, protect infrastructure and promote environmentally sustainable methods for managing wastewater. A summary of the major characteristics/advantages/disadvantages of each treatment type is presented in Table 12.

4.2 Desalination and de-chlorination

There are many types of desalination technologies to choose from to remove dissolved salts and other contaminants from water, each appropriate for various operating conditions and water types. Reverse osmosis (RO) is still the leading desalination technology globally based on the criteria of historical performance and efficiency. The reverse osmosis process uses applied pressure to push water through semi-permeable membranes, which allow water to pass through them while rejecting the salts and other contaminants in the water. However, although there have been numerous improvements to RO technology, some key limitations include high initial capital costs, high energy requirements, and several ongoing issues (membrane fouling, scaling, periodic replacements), all of which lead to increased lifecycle costs.[107]

Conventional thermal desalination technologies such as vapour compression, multi-stage flash and multi-effect distillation have been used for many years in areas that have high availability of thermal energy. However, due to the growing global focus on energy efficiency and reductions in carbon emissions, their use has declined because they depend on high temperature and energy consumption. There are many new and developing methods of desalination such as ion exchange, gas hydrate, electrodialysis, forward osmosis and nanofiltration, all of which may provide some advantages under certain conditions; however, many of them are limited by lack of technical development, scalability issues and cost. The primary disadvantages of the above systems are membrane damage, membrane fouling and operational complications. These

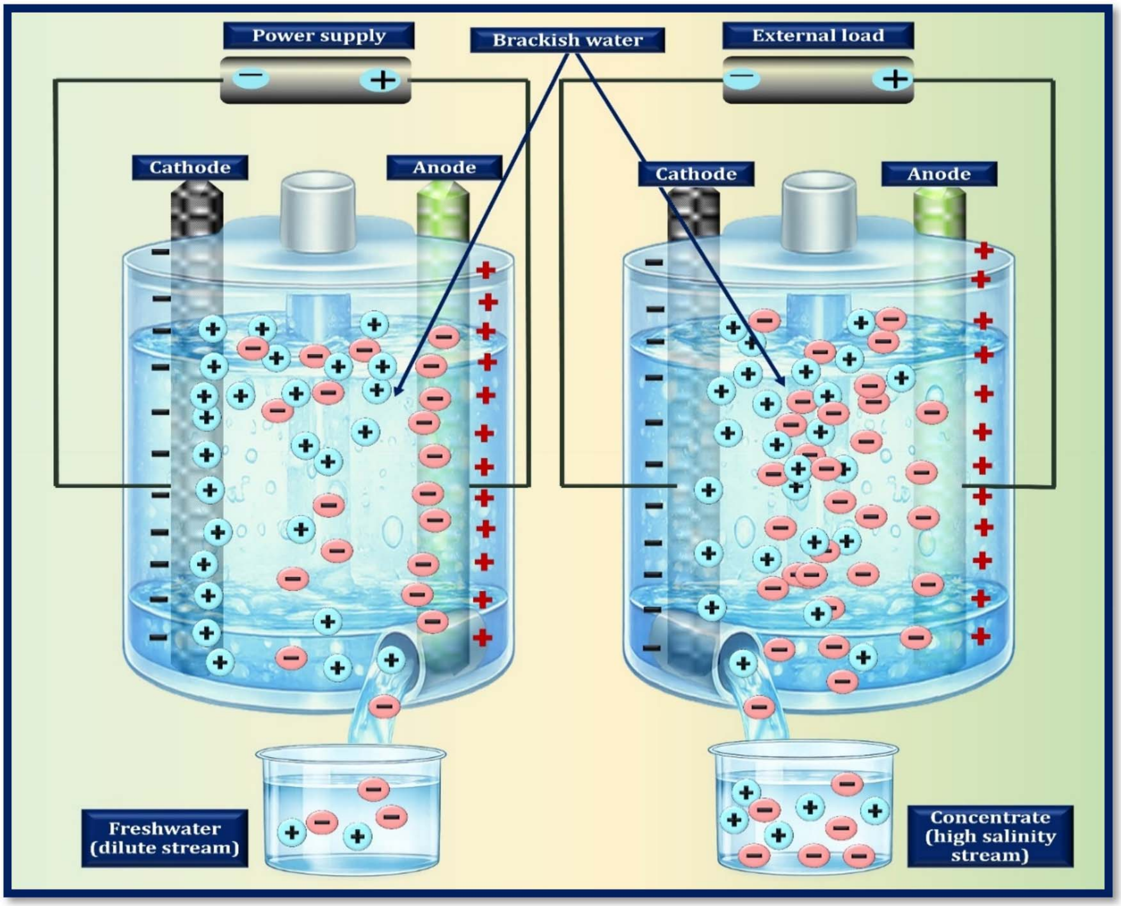

Fig. 13 Schematic illustration of capacitive deionization process.

factors are still causing barriers to the full-scale implementation of the above systems.[108]

Capacitive deionization (CDI) has received significant attention as a new method of desalinating water due to its many advantages, including low energy use, operation at normal temperatures & pressures, and no expensive membranes. As shown in Fig. 13 below, CDI operates by applying a low electrical potential (typically between 0.8 & 2 volts) to the water, which causes the dissolved ions in solution to migrate toward ionic, porous electrodes. Once at the electrodes, these ions will be stored in the electrical double layer (EDL) created by the charge at the surface of each electrode, much like how supercapacitors store charge. After the saturation point has been reached for the electrodes, they will then be regenerated by reversing the potential or removing the applied voltage so that they can be reused for many cycles.[109]

Electrode materials, system design, and operational efficiencies have been key focus areas for improvements in CDI technology in the recent past are shown in Fig. 14. High surface area, carbon-based materials such as activated carbons, carbon aerogels, graphene, and carbon nanotubes are now used to greatly enhance ion adsorption capacity and increase the efficiency of charge transfer. Hybrid CDI systems (for example, membrane capacitive deionisation (MCDI)) use ion-selective membranes to improve selectivity and reduce the expulsion of co-ions, thus improving overall desalination performance. Additionally, faradaic electrode materials such as transition metal oxides and conductive polymers are being researched for their potential to provide pseudo-capacitive or battery-like ion storage mechanisms, which result in even better salt removal capabilities. Although CDI has many positive attributes, it also faces multiple technical barriers to large-scale deployment, including limited salt removal capability when dealing with high salinity water (*e.g.* seawater), degradation of electrodes after extended use, and degraded performance due to competing ions and organic contaminants. Furthermore, ongoing research has demonstrated that optimising flow dynamics, reducing the amount of energy consumed and achieving long-term performance stability for the system will be necessary to facilitate the enduring growth of CDI systems.

Nonetheless, CDI has a lot of potential for some specific applications, like saline & marine water purification; industrial wastewater reuse & decentralised water purification systems. Furthermore, the fact that CDI is compatible with renewable energy (wind & solar) makes it an attractive option for sustainable desalination solutions. Continued research into material innovation and system integration will create even more importance for CDI as a tool to help address global Water Scarcity Challenges by lowering the Environmental Footprint of Conventional Desalination Technologies.[110]

4.3 Biological-AOP integrated treatment systems

It is common practice to combine biological methods with advanced oxidation systems in treating sewage as they target different classes of pollutants. Although inexpensive and highly efficient in the removal of readily biodegradable organics, biological processes cannot handle stubborner pollutants. Advanced oxidation techniques are able to decompose these pollutants because of their high oxidative power. However, they are relatively expensive. One such technique is the Fenton process, which combines oxidation and coagulation. Due to its dual nature, the Fenton process can be applied as pretreatment to biological methods.[111]

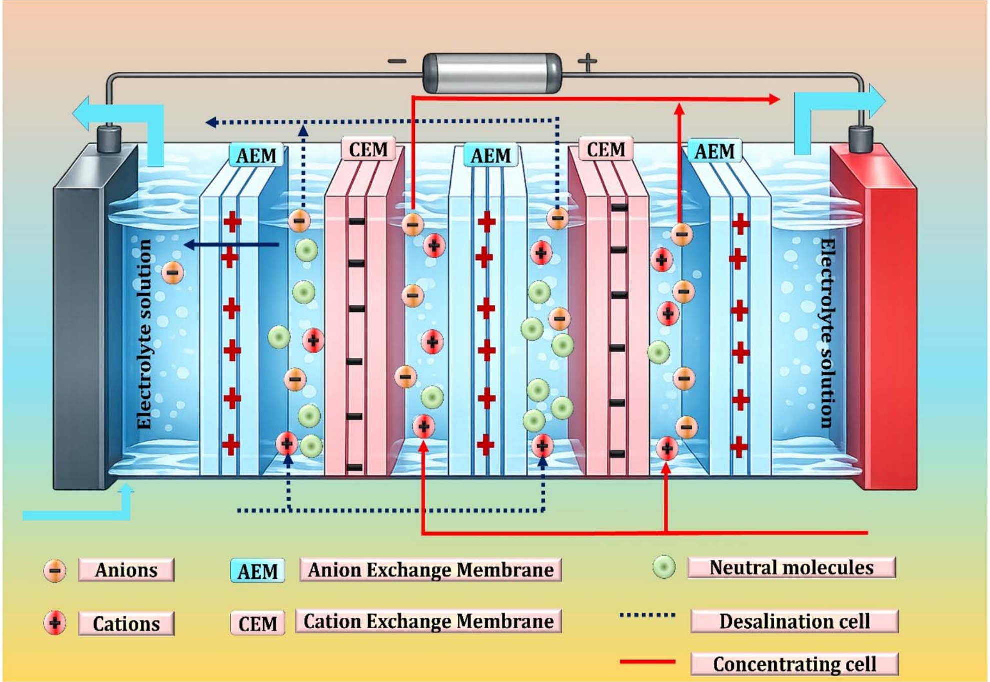

Fig. 14 Working principle of electrodialysis.

AOPs are technologies in which very reactive oxygen molecules decompose recalcitrant organic compounds into less complicated fragments or intermediates. This makes these molecules easier to degrade during biological processes. Hence, the combination of these treatment processes makes the water treatment process easy since there is enhanced biodegradability of organic contaminants through this combination. Moreover, AOPs can lead to partial degradation of organic compounds into minerals, reduction of toxicity, and changing of chemical structure of these contaminants to enhance microbial attack. It means that these processes complement each other due to their weaknesses. BIOPs have been ineffective in dealing with difficult pollutants while AOPs are quite expensive when applied alone. The combined technology makes it possible to eliminate these disadvantages and make the technology more cost-efficient. It also makes the treatment process easier, stable, and flexible in treating varying types of pollutants. Moreover, integration of these technologies may reduce the energy requirement, decrease the number of chemicals needed, and minimize secondary pollutant generation.[112]

While at the same time biological processes degrade oxidation byproducts produced during the advanced treatment process; they provide for good process stability as well as increased overall treatment effectiveness. The combination of these two methods allows for complete degradation of contaminants into harmless end products (*e.g.*, CO_2 and H_2O) whereas both methods keep costs down and decrease environmental impact. Additionally, interconnecting the oxidative and biological phases reduce the toxicity of the waste stream, which allows for a greater ability of the microorganisms to degrade the waste stream, while providing sustained long-term performance.[113] Electrocoagulation is a method of treating water in which the use of electrical current passed through sacrificial metal electrodes commonly made of aluminum or iron creates coagulant species *in situ*. The metal ions created in this manner react with water to produce metal hydroxides, which will neutralize the suspended particle's negative surface charge and cause the breakdown of the colloidal system. Thus there is a fusion of fine particles into large aggregates called flocs, which can be removed through sedimentation or flotation. Furthermore, in addition to removing solids, this technique can also trap dissolved organic and inorganic infectious substances within the floc structure. In addition to coagulation, electro coagulated water is also very good at disinfecting water. A reduction in microbial populations as well as a prevention of biofilm formation occurs due to the dual-action nature of the technology. This approach helps to eliminate both organic and biological fouling, which are two significant fouling problems associated with water treatment systems. The flotation formed by gas, such as hydrogen on the cathodes, also improves the flotation and thus the separation efficiency of the formed flocs.[114,115]

Research has shown that using electrocoagulation with aluminum electrodes can remove over 70% of dissolved organic matter and kill all microorganisms in saline water. Total suspended solids can also be removed with efficiencies of over 99% by electrocoagulation.[116] Electrocoagulation systems are easier to operate than conventional coagulation systems, require fewer chemicals, and produce less secondary sludge than conventional methods. The electrocoagulation mechanism includes:

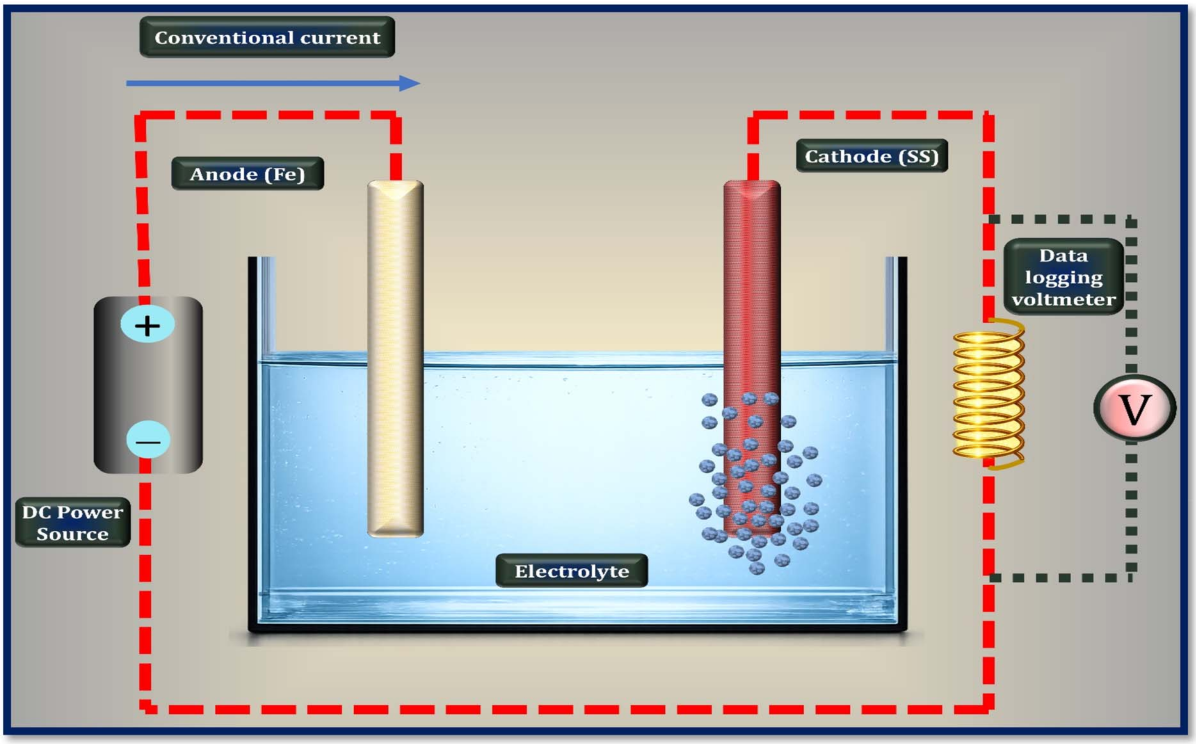

Fig. 15 Working mechanism of the electrocoagulation process.

electrode dissolution, floc formation, pollutant adsorption and separation as shown in Fig. 15.

5 Transforming every drop: a comparative analysis of water to-hydrogen strategies

5.1 Performance metrics: hydrogen yield and energy efficiency

As an alternate low-carbon energy carrier, hydrogen can help solve the depletion of fossil fuel resources and the effects of climate change. Hydrogen provides a viable substitute for a variety of conventional fuel applications. It has more than double the gravimetric energy density than typical fossil fuels (approximately 140 MJ kg^{-1} *versus* approximately 50 MJ kg^{-1}). Hydrogen can deliver energy in multiple ways; it is highly efficient to store; and it generates water as the only emissions from combustion.[117]

Hydrogen is the most plentiful substance in the universe, and it is a clean source of energy. However, hydrogen does not exist freely in large quantities within our planet; rather, it is usually found as part of compounds such as water (H_2O) and hydrocarbons. Thus, hydrogen requires manufacturing before it can be used. There are many manufacturing pathways available; some of them are represented in Fig. 16. However, hydrogen produced from renewable and low-carbon sources is considered fully sustainable. In this regard, the process for manufacturing "green" hydrogen at scale is through the electrolysis of water, which involves splitting water into its hydrogen and oxygen components using direct electric current. The cost of various methods to manufacture hydrogen varies greatly around the world, as summarised in Table 13, which provides a snapshot of worldwide data on cost-of-manufacturing hydrogen using water as a feedstock to create the hydrogen.

The hydrogen economy requires consideration of hydrogen storage, transportation, and end-use technologies in determining how we will use it. Hydrogen may be stored in three primary ways – compressed gaseous form, liquefied cryogenically (to temperatures lower than 253 degrees Celsius), or embedded in chemical carriers such as ammonia or metal hydrides. Each method has advantages and disadvantages depending on the applications. Similarly, transportation of hydrogen can occur by pipeline, tanker (trucks or ships), or by shipping in liquefied or carrier formats. Infrastructure issues and concerns for safety are significant barriers for widespread

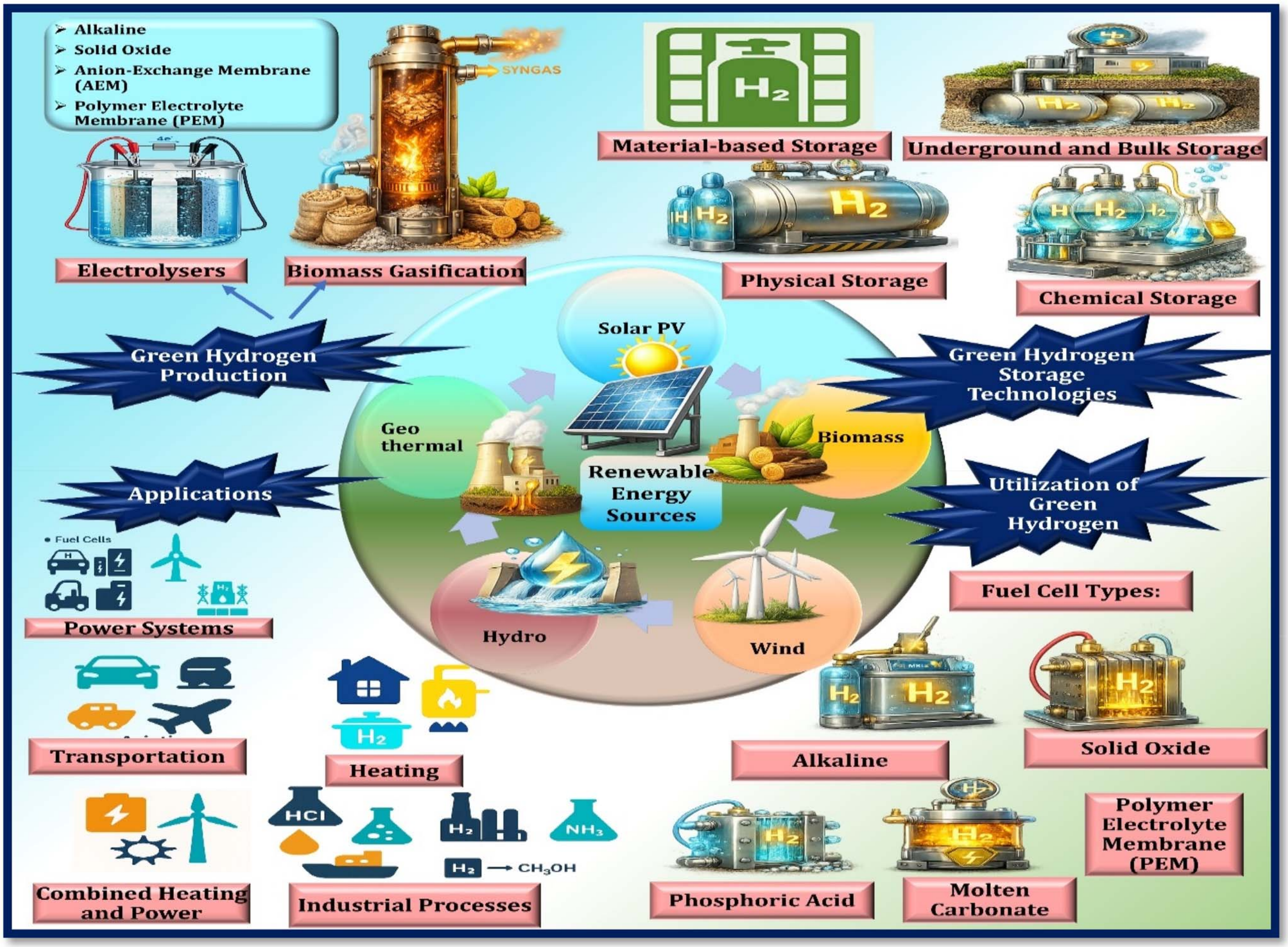

Fig. 16 Conceptual overview of sustainable hydrogen energy systems.

Table 13 Economic viability across the water-to-hydrogen spectrum: global case studies

S. no	Energy source	Electrolyser type	Hydrogen production rate	Cost of hydrogen (USD per kg)	Key insights	Ref.
1	PV-wind hybrid	PEM	25 vehicles per day	7.5–7.9	Renewable hybrid feasible but capital-intensive	119
2	Grid electricity	PEM/alkaline/ SMR	30–300 N m^3 h^{-1}	7.7–17.9	PEM slightly cheaper; SMR lowest at high scale	120
3	Wind	Alkaline	—	4.3–5.8	Favourable sites with low energy cost	121
4	Wind farms	PEM	—	3.37–9.0	Cost falls if using existing wind infrastructure	122
5	PV/geothermal	PEM	—	0.9–5.0	Lowest cost with full market penetration	123
6	Offshore wind	PEM	101 MW	5.0 € per kg	Offshore systems feasible post-2030	124
7	Wind	—	3.2–5.3 tonnes per year	—	Smaller turbines less cost-effective	125
8	—	PEM	30 N m^3 h^{-1}	16.4	Monte Carlo simulation for uncertainty evaluation	126
9	Geothermal + CO_2 storage	—	—	4.7–8.7	CO_2 utilization enhances energy recovery	127

deployment. Hydrogen also plays an important role in decarbonising hard-to-electrify sectors including heavy industry (*e.g.*, the manufacturing of steel, cement and chemicals) and long-range transportation modes (aviation, shipping, and heavy-duty trucking). Hydrogen can be used in fuel cells to efficiently generate electricity with high energy efficiencies and no tailpipe emissions, making it an attractive option for use as a clean energy carrier.[118]

The widespread use of electrolyser technology is hampered by many economic and technical barriers, such as high initial costs of an electrolyser; reliant on renewables for electricity; significant efficiency losses from production to use of hydrogen; poor material durability; and system life. In addition, large-scale electrolysis requires reliable access to appropriately treated water, while the dominant economic and technical challenge remains the high electricity demand associated with water splitting. Current research is concentrating on improving performance of the catalysts, increasing efficiency of electrolysers, including renewables into hydrogen production, and creating less expensive ways to store and move hydrogen long distances. Policymaking, creating infrastructure, and working together across borders are critical to move forward with hydrogen as an energy source. The overall goals of these goals will enable hydrogen to become an important part of the sustainable energy system of the future.

5.2 Environmental & economic evaluation

Due to factors like economic expansion, advances in technology, and population growth, energy consumption has increased due in great part to development–driven activity. In most nations developing their economies, increased energy demand is attributable to intense industrial development, continued urbanisation through migration from rural areas into urban centres and constructing infrastructure. In addition, increasing energy demand is also attributable to population growth in all sectors requiring energy for housing, transportation, and commercial activity. Although majority of the world has depended on fossil fuels to create modern society, continued reliance on these sources of energy is creating major environmental challenges due principally to CO_2 emissions, which has made them a major cause of climate change, and global warming.[128]

As an energy carrier, hydrogen is receiving a lot of interest as a clean and flexible option that could help support deep decarbonisation by providing energy for multiple sectors. Hydrogen can be produced from many different feedstocks including natural gas, coal, biomass and water through electrolysis – allowing for flexibility to use various resources to generate it. Hydrogen produced from renewable sources (such as electrolysis powered by solar or wind) can be generated with virtually zero emissions throughout its lifecycle, making it an important component of future sustainable energy systems. Examples of the hydrogen production feedsheets and their associated environmental impacts are illustrated in Fig. 17. Additionally, the type of resources and production technologies used to produce hydrogen varies significantly between some of the largest economies, primarily due to differences in the resources they have access to, their energy policies, technological maturity, and other economic factors. An example where certain large countries have significant amounts of natural gas buried beneath them, would lead them to continue to use steam methane reformation for producing hydrogen. Conversely, these same countries should see a greater emphasis on green hydrogen production as they develop their renewable energy infrastructure. Additionally, while there is still coal-based hydrogen production occurring throughout the world, it is mostly being produced in areas where the cost advantage and the pre-existing physical infrastructure exists, despite the significant carbon foot-print that goes along with it. Fig. 18 highlights the different methods being used to produce hydrogen around the world. However, moving towards hydrogen for energy requires many changes to how we produce and use now, this includes high costs, low energy efficiency for manufacturing, issues with storage and moving it, and the need for additional large projects. In order to make low-carbon hydrogen technologies more widely available and use them as

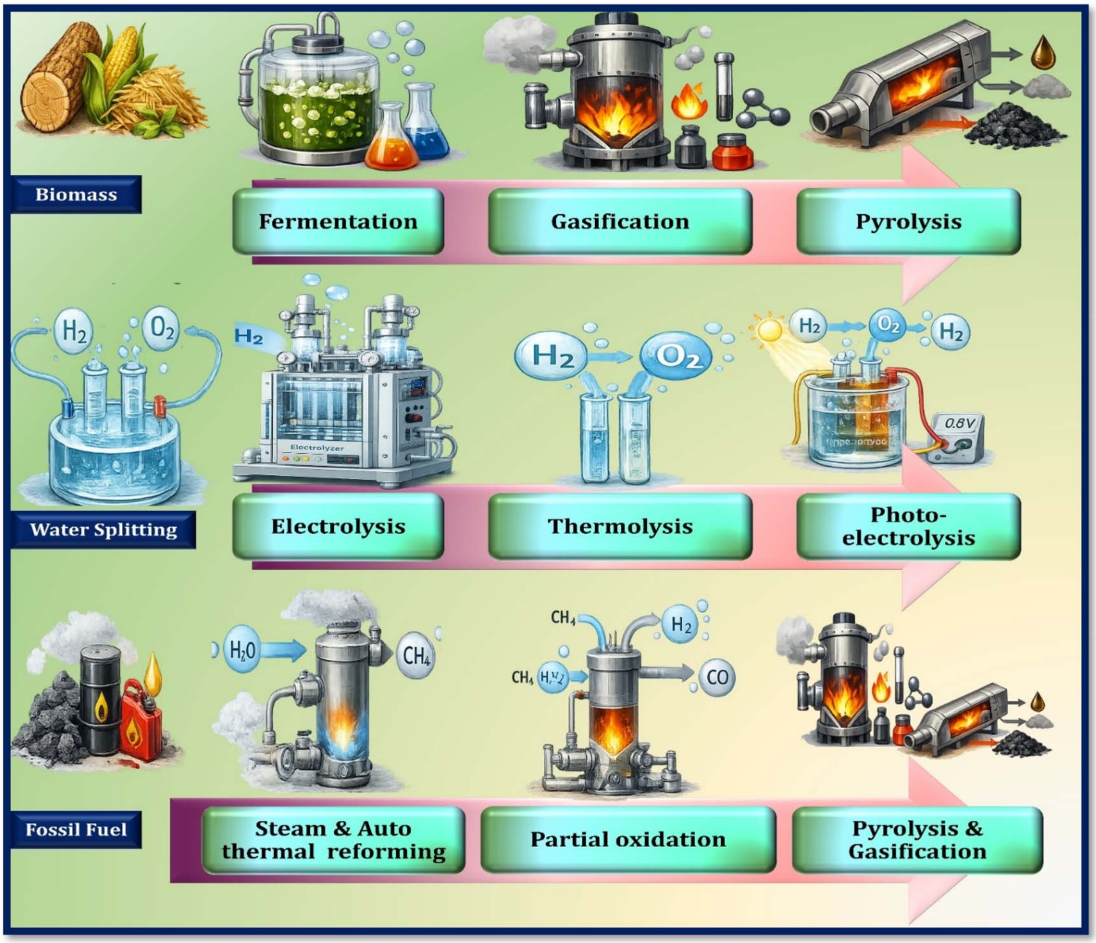

Fig. 17 Schematic representation of feedstock-based hydrogen production routes.

part of the worldwide energy system, governments, businesses and nations working together will be key.[129]

5.2.1 Life cycle assessment of hydrogen production.

A life cycle assessment (LCA) is an organized set of processes that can be used to quantify the environmental effects of any product, service, or system over their entire lifetimes. This begins at the stage of raw material extraction and processing and includes all levels in the supply chain until the product reaches consumers and ends up in a landfill or is recycled/disposed of properly. As hydrogen is recognized as an important clean energy carrier, evaluating hydrogen's total environmental impact through an LCA will help determine how much actual benefit or disbenefit exists through the use of hydrogen *versus* other energy carriers.[130]

Hydrogen is seen as a clean fuel because it doesn't produce emissions when used, but its sustainability relies on how it's produced. There are still a lot of traditional ways of producing hydrogen like gasifying coal or steam reforming methane but both of these create lots of carbon emissions. So there's now an interest in producing hydrogen using low-carbon or renewable energy sources, particularly *via* water electrolysis driven by solar PV or other renewables.[61] LCA-based methods are used to evaluate the environmental impacts, economic viability and scalability of hydrogen produced through various processes, so as to determine which process to use for particular hydrogen generating applications when taking into account both cost and sustainability are shown in Fig. 19.[131] Also, LCA-based assessments are made for hydrogen produced through storage, transportation and distribution, which can affect overall system performance. For example, using energy to compress or liquefy hydrogen before using it will use a lot of energy, and using pipelines or compatible materials for transporting hydrogen will also require careful consideration from both an environmental and technical perspective. Finally, the cost of constructing new infrastructure (*e.g.*, electrolyser fabrication, storage tanks and refuelling stations) will add to the total emissions produced and must be considered in all assessments using LCA data.

Hydrogen life cycle assessment is also significantly impacted and complicated by the choice of functional unit and system boundary used in the analysis. This is particularly true for hydrogen life cycle assessments in terms of reporting results on a per kilogram basis for hydrogen produced, per unit of energy delivered or per kilometre travelled in mobility applications, which changes the way results may ultimately be interpreted. By expanding system boundaries to other potential sources of the

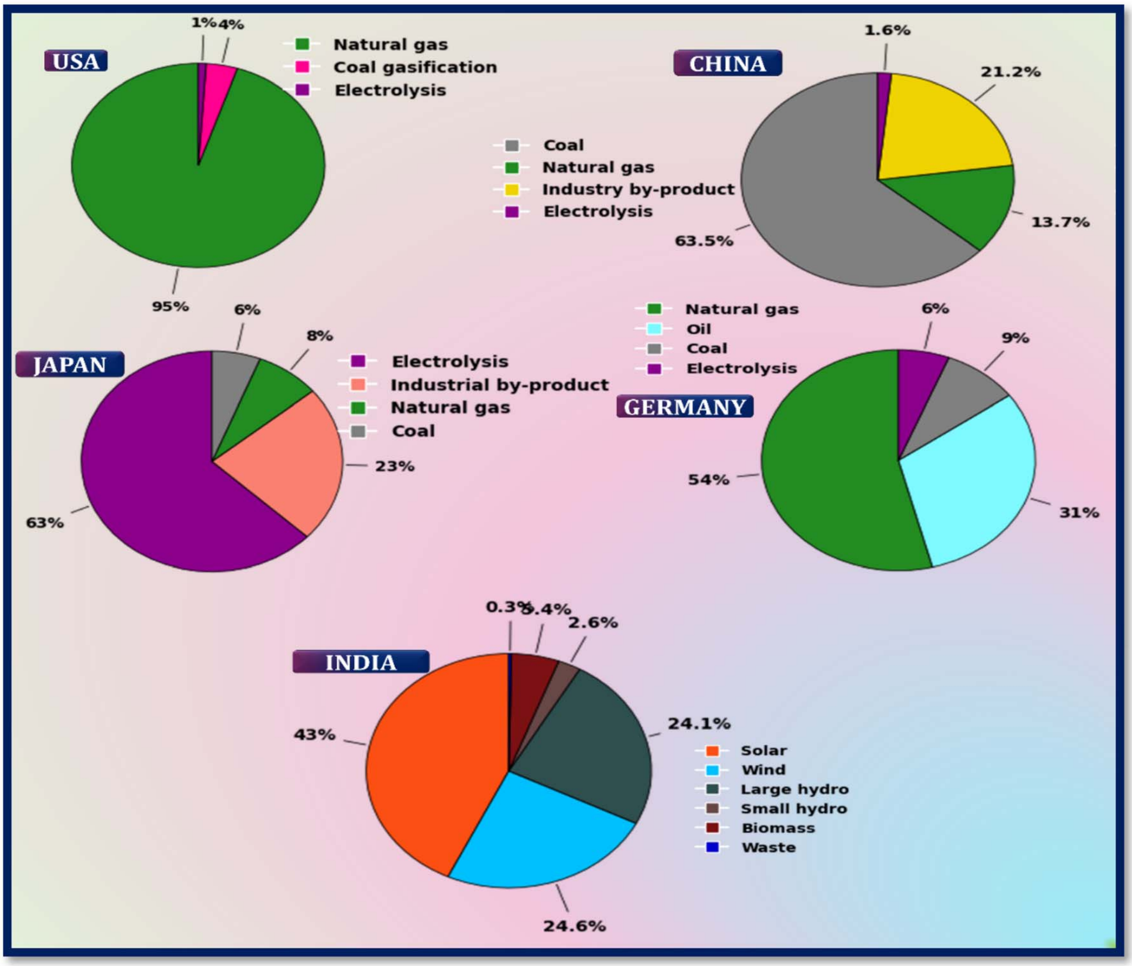

Fig. 18 Feedstock distribution for hydrogen production in leading global economies.

life cycle (*e.g.*, electricity generating facilities and both upstream and downstream treatments or uses of water) will provide for more comprehensive assessments of the life cycles of hydrogen production. Additionally, regional characteristics (electricity grid mix(s), availability of raw resources and technological maturity) will play a significant role in determining how the electricity used to produce hydrogen in each region is generated, adding further variability to reported hydrogen production life cycle assessments. The amount of water consumed and the amount of resources used are increasingly important for measuring the sustainability of hydrogen production and will continue to become even more critical as hydrogen production technologies develop. Water splitting utilizes relatively small amounts of high purity water (the feedstock) *via* hydrogen electrolysis systems; however, the amount of water required for the upstream treatment of the water as well as the amount of water used in upstream purification and cooling systems may increase overall process complexity and operational requirements. In regions with limited freshwater availability, alternative feedstocks such as seawater or treated wastewater, combined with suitable pre-treatment technologies, may improve long-term resource management and system resilience. The primary technical and economic challenge in water electrolysis is therefore not water availability itself, but the high electricity demand associated with water splitting and the associated energy conversion efficiency losses.[132]

In addition, LCA studies are being developed that will cover more than just greenhouse gas emissions and will now look at other environmental impacts, such as potential for acidification, eutrophication, human toxicity, and land use, *etc.* These types of assessments provide a more complete understanding of the trade-offs between hydrogen production pathways. For instance, a hydrogen production method *via* electrolysis using renewable electricity can result in a decrease in greenhouse gases, but it could require a greater amount of material for catalysts and components than other hydrogen production processes would. The combination of the LCA with TEA and policy frameworks is also imperative in helping guide large-scale hydrogen production. When considering environmental and economic aspects will allow individuals looking at hydrogen to determine the most cost-effective hydrogen production pathways while having the least negative impact on the environment. As the technologies used to produce hydrogen continue to evolve and improve, there must be harmonisation

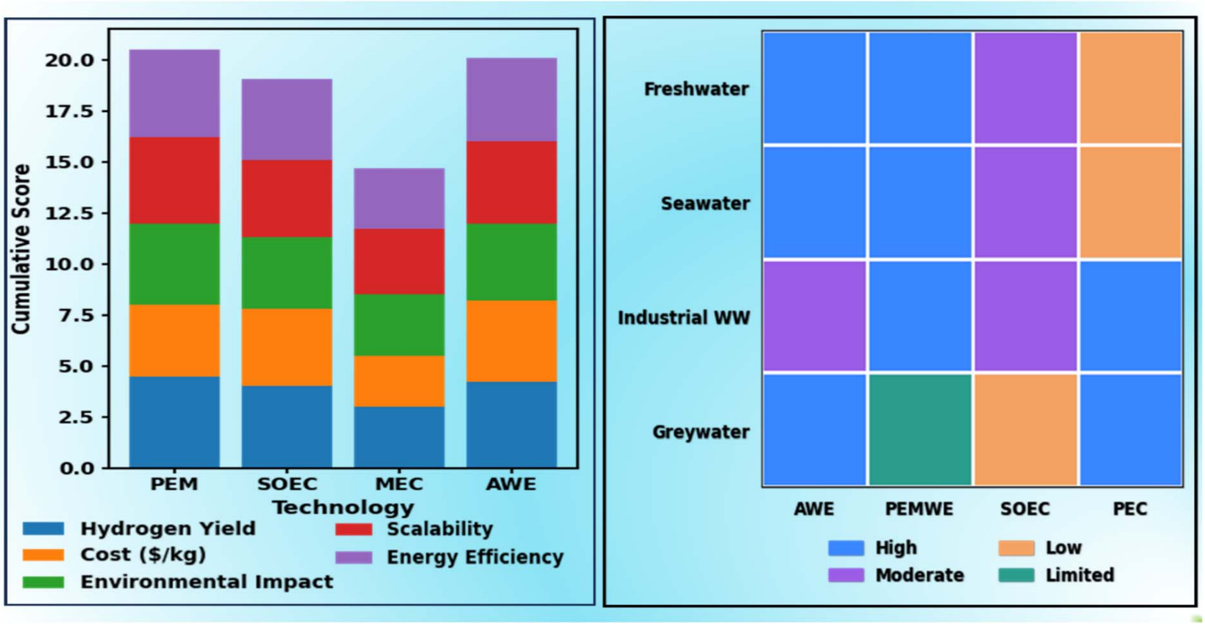

Fig. 19 Comparative suitability assessment of hydrogen production methods.

of LCA methodologies, standardisation of reporting practices, and up-to-date high-quality data, to ensure that individuals have the information needed for making consistent, reliable decisions.

From a thermodynamic perspective, the Gibbs free energy required for water splitting ($\sim$237 kJ $\mathrm{mol^{-1}}$ H_2 at standard conditions) defines the fundamental minimum energy requirement for hydrogen production. In practical systems, additional overpotentials arising from activation, ohmic, and mass transport losses significantly increase the actual energy demand beyond this theoretical limit, making electricity cost and efficiency the primary economic bottleneck rather than water consumption.[133] Overall, water quality and purification requirements are more critical to electrolyser durability and efficiency than the absolute quantity of water consumed during hydrogen production.

5.2.2 Life cycle assessment in water electrolysis. Ensuring the sustainability goals are reached requires lessening emissions and ensuring that hydrogen systems are economically feasible across the entire hydrogen system value chain. This includes a complete assessment of capital investment and operational costs associated with the construction of hydrogen production facilities to supply primary energy, hydrogen production technology, storage, transportation and end-use application. In addition to capital and operating costs, the availability of resources will need to be evaluated, particularly with respect to water usage because of increased demand for water due to deployment of large-scale hydrogen systems throughout the world, especially in arid/the United States with high density levels of people.[134]

Hydrogen produced through water electrolysis has been the subject of a number of recent life cycle assessment studies, with an increased emphasis on using appropriate functional units (*i.e.* kg H_2 produced or energy output) for environmental evaluation of the production of hydrogen. One large area of focus has been measuring the amount of energy consumed in the production of hydrogen using water electrolysis because the electricity required is by far the largest contributor to the overall environment footprint of electrolysis systems. Therefore, an important component of comparative studies on the different sources of electricity used by electrolysis systems (*e.g.*, fossil-based grid systems *vs.* renewable energy systems) has been determining how the different sources of electricity affect the amount of greenhouse gas emissions produced, energy efficiency of electrolysis systems, and overall cumulative environmental burdens of hydrogen produced.[135]

Photovoltaics are perceived to be a greater alternative to hydrogen production from fossil fuels because of their ability to produce hydrogen *via* low-carbon sources (*i.e.*, solar energy). When renewable energy is used to power electrolysis, it has been shown through several reviews that the GHG emissions throughout the entire lifecycle of the hydrogen will be about half the amount of GHG emissions produced when producing hydrogen using conventional methods such as steam reforming using fossil fuels. Determining the GHG emissions of PV electrolysis production *versus* those produced using conventional fossil fuels is contingent on multiple factors, including the GHG emissions associated with the upstream energy and materials to manufacture a PV module, the degradation rate of related PV and electrolyser systems, the land-use impact of renewable energy infrastructure, and the conversion efficiency of the PV panels and electrolyser used in the systems. If any of these are not taken into account, the benefits associated with producing hydrogen *via* electrolysis may be overstated.[136] Additional environmental impacts categories such as, the 'water footprint' of the production system, land used in the production system,

Table 14 Comparative life cycle insights into hydrogen production pathways

S. no	Technology	Energy source	LCA scope	GHG emissions	Main impact categories	Recommendations	Ref.
1	Cross-technology review (multiple systems)	Wind, hydropower, fossil-based systems	Review of published LCAs	Wind and hydro-based hydrogen have the lowest GWP; fossil-based routes have highest	GWP, acidification potential (AP), human toxicity	Broaden impact categories beyond GWP; prioritize renewables	137
2	AWE (alkaline water electrolysis)	Renewable and non-renewable electricity	Cradle-to-gate	Environmental performance highly dependent on electricity source	GWP, acidification	Improve lifetime and efficiency; prioritize renewable energy	138
3	PEMWE *vs.* AWE (comparative)	Mixed grid electricity	Cradle-to-gate	PEMWE showed lower environmental burden compared to AWE	GWP, resource depletion	Increase current density, use sustainable materials	139
4	SOEC (solid oxide electrolysis cell)	Nuclear energy	Cradle-to-grave	416 g CO_2 eq/kg H_2; low GHG, but high material toxicity	GWP, human toxicity, ionizing Radiation	Improve material sourcing, reduce radiation-related impacts	140
5	PEMWE (proton exchange membrane water electrolysis)	Wind energy	Cradle-to-grave	Major CO_2 reduction *vs.* NG; ozone depletion observed	GWP, ozone depletion	Renewable sourcing, material substitution	141
6	PEMWE	Grid mix/ Decarbonized	5 MW plant, Cradle-to-grave	89% GWP drop in decarbonized grid	GWP, resource depletion	Improve catalysts; deploy near renewable hubs	142

depletion of resources in the production system, and environmental toxicity created by the production system, have also been included in recent studies as a result of the expanding scope of current LCA research. One specific example of this is that the use of high grade water for electrolysis can require very significant amounts of energy to create pre-treatment for the hydrogen production, thus leading to greater energy use and increased use of chemicals. In addition, constructing a large-scale renewable energy infrastructure for hydrogen production may require transformation of land and greater amounts of materials, especially for the critical minerals that are necessary for constructing the PV panels and electrolysers. In addition, hydrogen systems can be integrated with other energy and industrial sectors, such as the following:

Hydrogen production with renewable electricity generation, as well as integrating hydrogen production with desalination, wastewater treatment work, or the recovery of industrial waste heat, can increase the efficiency of the entire system while also helping to reduce the overall environmental burden. For example, using recycled (*i.e.*, treated) wastewater (*versus* fresh water) for electrolysis can help alleviate water scarcity-related concerns, while using renewables to generate electricity that is put into an intermittent renewables system coupled to the hydrogen production process will help stabilize the grid and make use of energy more effectively. The viability of hydrogen production pathways will also depend significantly on economic and policy considerations such as:

- The carbon pricing system;
- Various incentives for renewable power generation, and;
- The continuing reduction of electrolyser manufacturing costs through technological advances.

Along with the economics of hydrogen production, the implementation of mass production, improvements in supply chain efficiency, and so on, will also drive down the levelised cost of hydrogen (LCOH) and make green hydrogen competitive against non-green hydrogen. Table 14 is a comparative synthesis of life cycle and environmental metrics for hydrogen produced through different methods, showing the trade-offs related to carbon emissions, resource use, and system efficiency. It is critical that comparative assessments are performed in order to assist in determining the conditions (region, technology) under which hydrogen production can be the most sustainable and easily scalable.

6 From bottlenecks to breakthroughs: identifying gaps in hydrogen production research

The main technical constraints in water-to-hydrogen systems are associated with energy efficiency, catalyst durability, membrane stability, and system integration rather than bulk water availability. Water electrolysis is fundamentally constrained by both thermodynamic and kinetic factors. The decomposition of water requires overcoming the standard potential of 1.23 V under ideal conditions; however, in real

Table 15 Classification and characteristics of catalyst poisoning mechanisms[145]

S. no	Type	Key idea	Effect	Reversibility
1	Geometric effect	Blocks active sites	Slows reaction	Reversible/irreversible
2	Electronic effect	Changes electronic structure	Affects kinetics	Irreversible
3	Selective poisoning	Attacks most active sites first	Rapid activity loss	Irreversible
4	Non-selective poisoning	Uniform surface coverage	Gradual activity decrease	Both possible
5	Reversible poisoning	Weak adsorption	Temporary loss	Reversible
6	Irreversible poisoning	Strong chemisorption	Permanent loss	Irreversible

systems additional voltage is required due to electrode polarization and ohmic losses.[143]

High-temperature electrolysis reduces thermodynamic energy demand by supplying part of the required enthalpy as thermal energy, thereby lowering electrical energy input. In contrast, low-temperature systems such as PEM and alkaline electrolysers rely entirely on electrical energy input, making them more sensitive to electricity price and efficiency losses.

Advances in electrolyser design, including membrane electrode assembly optimization and reduced ohmic resistance (as historically influenced by design concepts such as Zdansky-type configurations), have significantly improved current density and energy efficiency by minimizing internal resistance and polarization losses.[144]

Water-to-hydrogen technologies have made significant headway; however, a number of fundamental scientific and engineering obstacles remain that impede their widespread commercial implementation. Some of these continuing problems are the corrosion of electrodes, the scaling of the inorganic materials used in membranes, the fouling of the membranes, the deactivation of the catalysts, and the degradation of various components of the water-to-hydrogen systems. These problems are compounded by the increasing use of complex feedstocks (*e.g.*, seawater or wastewater) where the presence of multivalent ions, organic contaminants, and microorganisms cause accelerated degradation of materials and interfere with electrochemical reactions. Moreover, the substantial amount of energy required for feedwater pre-treatment processes such as desalination, filtration, and removal of contaminants can significantly decrease the overall energy efficiency and economic feasibility of the entire water-to-hydrogen conversion process. Accordingly, current research is increasingly focused on reducing energy consumption and improving materials durability rather than addressing absolute water availability. There is a general lack of pilot-scale and long-term demonstrations conducted under actual operating conditions; therefore, our understanding of system performance (particularly regarding stability, maintenance requirements, and lifecycle performance) is still insufficient. There is also a variability in the composition of water that introduces uncertainty in how these systems operate, necessitating adaptive control strategies and robust design of these types of systems.

The major issues are the lack of standard protocols for measuring and reporting on hydrogen production rates and on energy efficiency and durability measures, leading to complications in the comparisons of different research studies that contribute to the delay of technology development and commercialisation. In addition to this, there are issues relating to the integration of these systems with intermittent renewable energy sources, thermal management and gas purification, adding further complexity to these technologies. Furthermore, there are also economic and environmental factors involved with these technologies, involving costly and/or rare catalyst materials and associated infrastructure costs, and the handling of waste and/or off-gas from each system must be addressed in order for them to be sustainable. Advances in water-to-hydrogen technology development will require not only advances in materials and processes but also standard testing frameworks, scalable architecture and integrated systems that can operate effectively in a range of realistic and variable conditions.

6.1 Catalyst deactivation and poisoning mechanisms in water electrolysis

Understanding the factors that lead to catalysts being deactivated and designing catalysts that last as long as possible is necessary for designing catalysts to last longer (as shown in Table 15). These factors can be grouped into three categories: Chemical, physical, and kinetic. The interaction of these three types of deactivation based on the combined deactivation mechanisms are illustrated in Fig. 20. Each of the various mechanisms of catalyst deactivation fall into chemical, physical or kinetic categories based upon how physical chemistry reactions (catalyst reaction), kinetics (reaction rate) are impacted by chemical deactivation. The most common chemical forms of catalyst deactivation are through poisoning, fouling and under desirable side reactions; in all of the chemical deactivation scenarios the chemical activity of the catalyst is hindered in one way or another. Catalysts can be chemically poisoned when trace impurities (sulfur, nitrogen and chlorine, *etc.*) within the feed strongly adsorb on to the active sites of the catalyst, limiting the availability of these active sites for the intended reaction. In some cases, the physical adsorption of the impurity will have a permanent impact on the activity of this specific catalyst, reducing its capability. Another example of a catalyst that is chemically impacted by deactivation is fouling, which occurs when carbonaceous deposits or other by-products accumulate on the active sites of the catalyst, thus reducing the ability of the reactants to reach that active site. The physical category of these three catalyst deactivation factors also deals with sintering, which occurs when the temperature of the catalyst is raised and causes the small metallic particles that are responsible for catalyzing the reaction to coalesce into larger

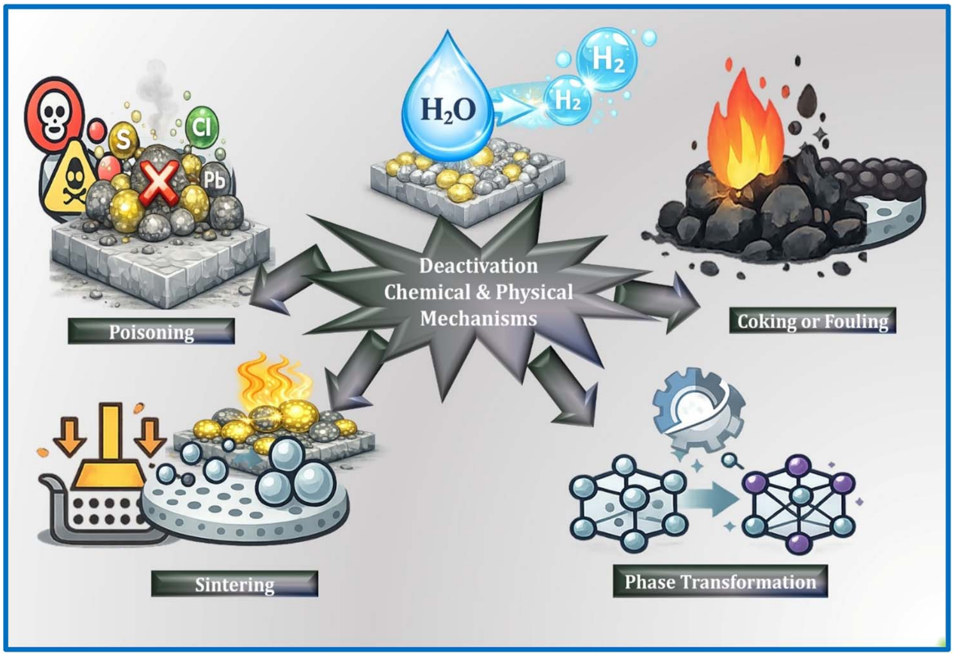

Fig. 20 Classification of major catalyst deactivation mechanisms.

particles, and therefore reduces the total surface area (and therefore the number of available active sites) available for catalyzing the reaction. Physical degradation from the support (*e.g.*, mechanical changes or structural collapsing of the support will further degrade the activity of the catalyst by reducing the number of active site and the pore size of the catalyst).

Kinetic elements are essential contributors to deactivation as changes in the diffusion-limited reaction rates, especially in a porous catalyst, can generate concentration gradients between active sites. Long-term run times at severe conditions may also change the reaction path making the generation of deactivation species (*i.e.*, cokes) occur more frequently. In summary, catalyst deactivation represents a complicated phenomenon that arises due to interactions of chemical contaminants, structural instabilities, and transport limitations. In order to overcome these problems, proper design of catalysts, development and optimization of operating conditions, and implementation of efficient regeneration or cleaning procedures are all necessary to restore catalyst reactivity.

While much work has been done to look at laboratory effects from contaminants related to catalyst poisoning, and while a large body of literature exists to confirm these effects through experimental work, harmonized testing methods do not exist today as a means of determining whether or not performance is the same while performing operations in either real or industrial wastewater electrolytes. In fact, significant discrepancies can be observed in the reported data with respect to catalyst performance due to variations in both the nature of the catalyst materials and the operating conditions, as well as the highly complex and variable nature of the various constituents present within the water being tested. This lack of consistent and accurate quantitative data makes it nearly impossible to make meaningful comparisons of catalysts with respect to their ability to resist poisoning and/or make comparisons on an electrochemical basis (exchange current density, Tafel slope, charge transfer resistance, *etc.*). Water streams that contain wastewater include a wide variety of different contaminants including dissolved salts, heavy metals, organic compounds, surfactants, and/or suspended solids and each of these contaminants can interact with the catalyst surface in various ways (*i.e.* site blocking, surface reconstruction, competitive adsorption, and/or irreversible chemical poisoning) and disrupt the catalytic activity of the catalyst thereby reducing catalytic efficiency and the stability of the catalyst during continued operation. Finally, synergistic or antagonistic reactions among multiple impurities can significantly increase or decrease the effects of deactivation thereby significantly increasing the complexity of determining the extent of catalyst deactivation and subsequently comparing performance to that identified in the laboratory. This complexity has rarely been addressed in simplified laboratory studies.

Lack of standardized testing metrics and durations is another major problem. Most studies look at short term operation under controlled conditions which cannot effectively capture the long term performance durability of catalytic systems or real world conditions as actual use would be experienced. In addition, there are also large variations between studies with regard to the preparation of the electrolyte solution, level of impurities in the material, pH, temperature, and current density which will further complicate reproducibility of a single study's results and comparability between studies.

In Table 16 the most recent studies on catalyst deactivation caused by impurities are compiled and systematically compared to produce a summation of current knowledge related to this

Table 16 Impact of common waterborne impurities on catalyst performance in electrolysis

S. no	Impurity type	Example source	Effect on catalyst/HER	Mechanism	Ref.
1	Sulfur species (H_2S, $SO_4{}^{2-}$)	Industrial gases, impure water	Strong poisoning; large drop in HER rate and current density	Site blocking, electronic effects	146
2	Arsenic (As^{3+}, As^{5+})	Groundwater, minerals	Increases overpotential; lowers current density	Chemisorption on weakly bound H sites	147
3	Cyanide (CN^-, HCN)	Metal plating waste	Raises Tafel slope and resistance; severe deactivation	Formation of metal cyanide complexes	148 and 149
4	Cations (Ca^{2+}, Mg^{2+}, Na^+)	Tap/river water	Higher overpotential; gradual activity loss	Surface fouling and scaling	150 and 151

area of research. The table groups the different types of impurities, their mechanisms of deactivation, and a qualitative severity rating of how severely each impurity would affect performance under different experimental conditions. This systematic framework establishes the knowledge gaps present today and identifies the urgent need for standardized methodologies and performance metrics to improve the future evaluation and development of catalysts that are designed to produce hydrogen from the processing of wastewater.

6.2 Membrane fouling and degradation

Membrane fouling usually describes the locations and ways that contaminants may form from places and methods that accumulate contaminants. Three general categories of membrane fouling can be identified: internal fouling (usually "pore blocking"), external (surface) fouling, and concentration polarization. Internal fouling usually occurs when dissolved matter and fine particles penetrate into the membrane and become accumulated or plugged into the porous media (membrane) itself; while external (surface) fouling typically occurs on the membrane surface where insoluble solids, macromolecules or colloids may deposit and form a discrete layer. The surface accumulation may subsequently develop into a gel or cake layer, depending on whether macromolecular adhesion is responsible for the fouling or if it is due to particulate accumulation on the membrane. Transmembrane pressure differential will mainly cause the formation of these layers by forcing the solutes and particulate matter towards the membrane interface.

Concentration polarization is a related but different phenomenon, which occurs when solutes and ions become concentrated in a boundary layer adjacent to the surface of the membrane during filtration. This increase in solute concentration at the interface results in an additional resistance to mass transfer thereby reducing permeate flux. The degree of concentration polarization is largely dependent on the hydrodynamics of the system, particularly the shear forces at the membrane; thus, high crossflow velocities can alleviate this issue by promoting back-diffusion of solutes and/or preventing accumulation of solutes.[152] The combined effects of material characteristics and operating parameters that influence fouling behaviour are generally captured in Table 17.

From both a cleaning and an operational standpoint, fouling can also be classified based on the reversibility of the type of fouling. Reversible fouling involves deposits that can be removed using physical means, such as hydraulic flushing, backwashing, or shear induced detachment (crossflow). Irreversible fouling consists of strongly attached or embedded contaminants that need chemical cleaning for their removal

Table 17 Influence of material and process variables on membrane fouling

S. no	Factor	Mechanism	Effect on fouling	Ref.
1	Material type	Organic *vs.* ceramic/metal membranes	Organic membranes foul faster; ceramics resist clogging and heat	153
2	Hydrophilicity/hydrophobicity	Surface energy and contact angle influence pollutant adherence	Hydrophilic surfaces reduce early fouling; hydrophobic surfaces trap organics over time	154 and 155
3	Surface charge	Electrostatic interactions with charged pollutants	Like-charged (negative–negative) surfaces resist contaminants, slowing fouling	156
4	Pore size & distribution	Regulates particle entrance and flux resistance	Larger pores cause quicker fouling, whereas smaller pores result in slower fouling but greater TMP	157
5	Porosity & roughness	Surface texture traps or repels particles	High roughness causes fouling, whereas smoother surfaces stay cleaner for longer	158
6	Module structure	Flow dynamics rely on membrane orientation	Vertical modules improve shear and minimise cake accumulation	159 and 160
7	Flux & TMP	Driving force for filtration	High TMP or flux accelerates fouling and shortens cleaning cycles	161
8	Temperature	Affects viscosity and microbial activity	Moderate temperature reduces EPS formation; low temperature increases fouling	162

and may not be able to be completely removed. Generally, loosely attached layers of material will be associated with reversible fouling, while blocking of pore space and the presence of strongly adsorbed species will contribute to the irreversible decline in performance. In addition to these classifications, membrane fouling can also be classified based on the type (nature) of the foulant: organic fouling; inorganic foulants (*e.g.*, scaling); biofouling; and particulate fouling. Organic fouling results from the adsorbed (in the pores or on the surface) natural organic matter (NOM), proteins, oils and surfactants that are subjected to membrane surfaces and modify their hydrophobicity and charge. Inorganic fouling, or scaling, occurs when the sparingly soluble salts precipitate and deposit on the membrane's surface, including calcium carbonate, calcium sulphate, and silica, especially at high recovery or supersaturated conditions. Biofouling occurs when microorganisms attach and grow on (biofilm development), and are therefore highly resistant to cleaning and will significantly reduce the performance of the membrane. Particulate fouling is caused by the accumulation of suspended solids and colloids.

Fouling develops in stages the initial stage is rapid pore plugging or adsorption, followed by the formation of a layer on the surface of the membrane, and finally, at the quasi-steady state, deposition and removal of foulants are generally balanced. Many factors influence the progression of fouling including membrane properties (pore size, surface roughness, hydrophilicity, and charge), feed water properties (pH, ionic strength, and concentration of foulants), and operating conditions (pressure, temperature, and crossflow velocity). Combating fouling involves using a combination of strategies at the material and process level. Common pre-treatment methods to reduce the amount of foulants prior to filtration through the membrane include coagulation, flocculation, adsorption, and media filtration. Membrane surface modifications can also be made to increase anti-fouling characteristics; these include hydrophilic coatings, zwitterionic materials, and nanoparticles. Optimizing crossflow velocity, implementing periodic relaxation/biofouling/backwashing, and controlling recovery rates are also important methods of reducing fouling. Ultimately, understanding the interactions among the mechanisms of fouling, foulant characteristics, and operating conditions is critical for increasing the lifespan of membranes, maintaining a stable flux of water, and decreasing energy costs and maintenance needs for membrane-based treatment systems.[163,164]

6.3 Challenges in scaling hydrogen production from wastewater

Although significant advances have been made under controlled laboratory environments, the majority of studies on hydrogen generation on wastewater is limited to bench-scaled or simulation experiments, which feed on synthetic feed streams and highly controlled operating conditions.[165] These findings have yet to be translated into real-world

Table 18 Current research status and scaling challenges in hydrogen production from wastewater

S. no	Technology	Catalyst/material used	Efficiency/key factors	Main advantages	Challenges/limitations	TRL/scale	Ref.
1	Solar hybrid electrochemical system	—	• Evaluated wastewater treatment • H_2 productios • System utility	Zero or low carbon emissions	High capital & operational costs	Lab scale	166
2	Alkaline hydrogen oxidation	W–Mo–Co–Cu–Ni alloy synthesized *via* electrodeposition	Multi-element alloy optimizes hydroxyl adsorption	• Non-precious alloy • High activity	Requires further validation	Lab scale	167
3	Microbial electrolysis cell (MEC)	Various bio-anodes/cathodes	Achieved TRL 6 using domestic & urban wastewater	• Renewable biohydrogen • Sustainable	Limited data on large-scale cost	Pilot	168 and 169
4	Electrolysis with wastewater	—	Laboratory H_2 purity analysis	Promising lab results	Needs pilot-scale validation	Lab scale	170
5	Alkaline hydrogen generation	Pt-based nanoclusters on N-doped supports	Strong Pt–N coupling enhances HER rate	• High catalytic activity • Efficient HER	Cost of Pt & scalability	Lab scale	171
6	Photocatalysis/photo electrocatalysis	Various semiconductor electrodes	10% solar-to-H_2 efficiency (with PV up to 83%)	Renewable-powered	Catalyst & electrode cost	Conceptual	172 and 173

applications, mainly because the real-world wastewater matrices are complicated and highly variable. The changes in organic load, suspended solids, dissolved salts, heavy metals and microbial content present operation uncertainties and further variations in pH, temperature and salinity make the stability and performance of the system even harder to predict.[166] These issues have a serious impact on the electrode durability, catalyst activity, membrane intactness, and the system efficiency. Specifically, the effects of fouling, scaling, or corrosion are exaggerated in the real conditions with wastewater and their consequences eventually result in a decrease in performance. Furthermore, the efficiency of hydrogen evolution and the expenditure of energy can be diminished by the presence of competing redox-active species and enhanced. Consequently, there is a dearth of long-term operational data under realistic conditions and this restricts the capacity to reliably assess lifecycle performance, maintenance needs and economic viability.

The other important impediment is the absence of standardized pre-treatment methods to satisfy the various types of wastewater, including municipal, industrial, and greywater streams. Pre-treatment requirements like filtration, coagulation, biological treatment or desalination complicate the overall process, increasing its cost, as well as energy requirements, which could negate the sustainability advantages of hydrogen production. In addition, the connection of these systems to renewable sources of energy, *e.g.* solar or wind, also presents new intermittency issues that need to be resolved by designing the system and implementing energy management strategies. In order to seal these gaps, there has been an increasing demand to have integrated pilot-scale systems integrating wastewater treatment and hydrogen generation in one setup. To ensure process robustness, system configuration optimization, and generate reliable performance information, field demonstrations in various operational environments are necessary. Comprehensive techno-economic analysis (TEA) and life cycle assessment (LCA) to assess the consequences on the environment, resource efficiency, and cost competitiveness compared to traditional hydrogen production pathways should also be taken into account when conducting such studies. As can be observed in Table 18 most of the technologies reported are still in their early development stages (technology readiness level ≤ 6) and as such are still waiting to pass beyond laboratory validation. This highlights the importance of interdisciplinary cooperation between the researchers, industry stakeholders, and policymakers in order to facilitate scale-up, standardization, and commercialization. The solutions to such challenges will be essential in unlocking the potential of wastewater as a sustainable and circular resource to produce green hydrogen.[174,175]

7 Conclusion

The All Water to Hydrogen model offers a completely novel approach to the concept of sustainable fuel production as it connects hydrogen generation to overall use of water resources. This paper has analyzed recent advancements in the electrochemical, thermochemical, and bio-electrochemical approaches that can convert a broad spectrum of water sources, such as, potable water, saline water and wastewater streams into hydrogen. The analysis supports the claim that with a combination of powerful pre-treatment methods, appropriate material selection, and optimization on the system-level, it is possible to adapt various water qualities to the production of hydrogen. Existing data points out that the most technologically developed methods of operation are electrolysis-based, especially when coupled with renewable energy sources. Meanwhile, new process designs like microbial electrolysis systems and light-assisted catalytic methods show the possibility of using energy recovery with concomitant water purification. Although these advances are made, there are a number of barriers that have not been addressed. The dominant technical and economic challenges are associated with the high electrical energy demand of water splitting, long-term material degradation, membrane stability, and efficiency losses during operation. In comparison, the overall water consumption associated with electrolysis is relatively modest, although feedwater quality remains important for preventing catalyst poisoning, membrane fouling, corrosion, and durability loss, particularly in PEM-based systems. The major concerns are material degradation during long operation period, energy consumption during feedwater conditioning and the challenge of sustaining performance during variable and contaminated water conditions. Moreover, the majority of the available research is confined to designed environments or early prototypes, with the need to have a bigger validation and long-term operation testing. Continued advances in catalyst development, membrane operation, and energy integration with renewable sources reinforce the viability of deploying this concept to scale. In addition, thermochemical cycles and industrial by-product hydrogen recovery pathways may provide complementary strategies for improving hydrogen availability while reducing energy consumption and industrial emissions. These technological advances also lead to the creation of integrated water-energy cycles, which could help solve several issues faced by the world such as freshwater shortage, environmental pollution, and clean energy requirements. The most important step to take in the future is to make sure that engineering design, environmental considerations, material development, and policy development are moving hand in hand. Pilot-scale operations, common performance metrics, and detailed economic/environmental assessment procedures will be essential steps on the way to commercialization. Essentially, the concept propagates the notion that any types of water irrespective of source and quality can be used as a potential input to hydrogen production. However, successful implementation will depend primarily on improving energy efficiency, reducing electricity costs, enhancing electrolyser durability, and developing scalable integrated treatment systems for diverse water sources. To achieve this vision, it will rely on the long-term innovation, investment, and regulatory encouragement to make sure that hydrogen technologies will not only provide climate advantages but also enhance water sustainability and ecosystem resilience.

Conflicts of interest

The authors declare no conflict of interest.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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