Position Paper

Hydrogen Europe Research

Alternative hydrogen production processes

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November 2025

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Abstract

The transition to a sustainable hydrogen economy remains constrained by the limited share of low-emission hydrogen production, with conventional carbon-based processes dominating current supply. Conventional water electrolysis, on the other hand, is not the most viable alternative in all use cases. This review provides a comprehensive overview of alternative hydrogen production pathways, focusing on electrochemical, photolytic, and biomass-based processes. Depolarized electrolysis, including SO_2 and nitrogen-compound-assisted methods, offers lower energy requirements and the potential for co-production of value-added chemicals. Biomass-based approaches, such as two-stage anaerobic digestion, pressurized pyrolysis, and thermochemical cycles, enable decentralized, renewable hydrogen production while valorising waste streams. Photolytic methods, including photoelectrochemical and photocatalytic systems, mimic natural photosynthesis to directly convert solar energy into hydrogen, offering long-term sustainable solutions. Despite promising advances, these technologies face challenges including catalyst development, system scalability, feedstock variability, process integration, and techno-economic feasibility. By mapping current research, pilot-scale demonstrations, and knowledge gaps, this review highlights the potential of alternative hydrogen production processes to complement conventional electrolysis, diversify supply chains, and support a resilient, flexible, and decarbonized hydrogen economy.

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Introduction

Despite significant efforts by authorities, funding agencies, and researchers to advance a clean hydrogen economy, less than 1% of the produced hydrogen is obtained through low-emission processes, according to the latest IEA report[1]. Many of the most economically viable "clean" alternatives currently involve carbon capture technologies applied to traditional methods, rather than fully sustainable processes.

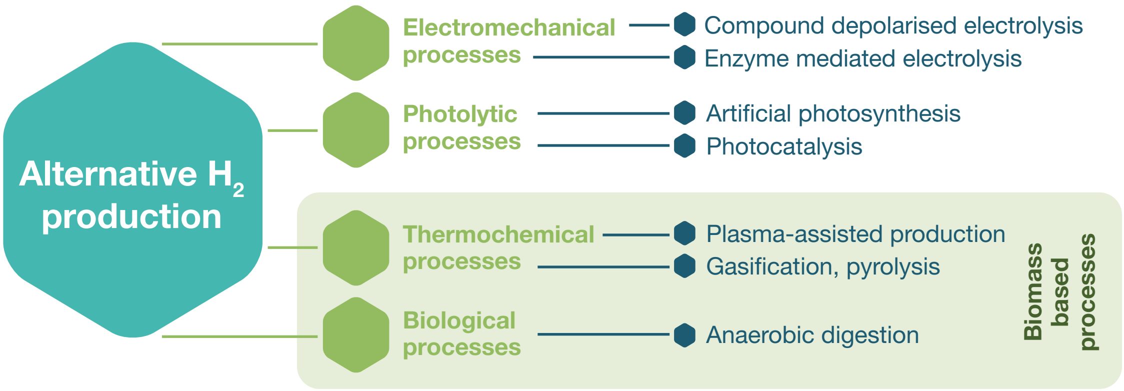
A more effective way to address this challenge is to recognize that, particularly in the energy and mobility sectors, there is rarely a one-size-fits-all solution. Instead, a spectrum of coexisting technologies is required to collectively achieve a shared goal—in this case, a versatile, reliable and scalable supply of clean hydrogen.

This report presents the current state of the art, challenges, and future development needs for selected alternative hydrogen production methods. It is organized into three main categories (Figure 1):

- **Electrochemical Processes:** Involving feeding compounds - other than water - into electrochemical cells. While the fundamental hydrogen production remains unchanged in comparison to water electrolysis, the altered reaction pathways lower energy requirements and potentially produce additional value-added products.
- **Photoactivated Processes:** Aiming to replicate naturally occurring phenomena such as photosynthesis, utilizing solar energy directly for hydrogen generation.
- **Biomass-Based Processes:** In these methods, hydrogen stored within organic compounds is extracted through gasification or pyrolysis or via biological pathways such as bacterial digestion and hydro-genesis.

Each of these alternatives offers unique opportunities for expanding hydrogen production into sectors where traditional water electrolysis may be impractical or economically not viable.

Figure 1: **Classification of alternative clean routes for hydrogen production**



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Current state of research

2.1 Electrochemical processes

2.1.1 Compound-based depolarized electrolysis

Compound-based depolarized electrolysis, has the potential to reduce both the energetic costs and mitigating the overall product costs by obtaining valuable by-products. This approach to water electrolysis relies on the introduction of a compound – other than water – into the anode, therefore altering the anodic reaction, without modifying the cathodic reaction (HER). Theoretically, any oxidation reaction that releases protons could be used to "depolarize" the anode on a water electrolysis cell, without altering the cathodic HER, though the main alternative currently studied is the SO_2 depolarized electrolysis (SDE). In SDE, the oxygen evolution reaction (OER) is replaced by the SO_2 oxidation reaction (SOR), reducing the theoretical voltage from 1.23 V to 0.158 V vs RHE, replacing the O_2 by H_2SO_4 in the anode. In spite of being the most researched alternative, SDE still is currently in early stages of development. Current state of the art studies[2–4] are all carried out on either fuel cell or electrolysis components, slightly adapted to operate under SDE conditions. Consequently, the concept of a SDE stack arrangement has not been designed or proposed, the optimization of the specific components for SDE is a necessary step to achieve the established targets from the DoE of 500 mA/cm^2 at 1.0 V with a concentration of H_2SO_4 of ≥ 50%, which would position the SDE-sourced H_2 as economically competitive with natural gas derived H_2[4].

Another promising approach for OER replacement in electrolysis involves the oxidation of aqueous solutions containing N-based compounds, where a N-compound reacts instead of O_2. This approach offers significantly lower theoretical energy requirements compared to conventional water splitting: 0.057 V *vs* RHE for ammonia, – 0.334 V *vs* RHE for hydrazine, and 0.072 V *vs* RHE for urea. These nitrogen-containing compounds are attractive due to their high hydrogen content and good solubility in water[6–8]. Ammonia, a carbon-free compound, is produced on a large scale and can be readily liquefied and transported over long distances, making it a practical hydrogen carrier. Urea is a cost-effective and widely available compound with a well-established production infrastructure. The electrochemical oxidation of hydrazine is particularly attractive because it generates nitrogen gas without forming any carbon-containing by-products - unlike urea - although hydrazine is toxic and highly reactive, its hydrate form is non-flammable, making it comparatively safer to store and manage under controlled conditions[9].

The concept of methane/natural gas-assisted electrolysis has also been proposed as a method to enhance the efficiency of solid oxide electrolysers (SOECs) and molten carbonate electrolysers (MCEC) thereby enabling more competitive syngas production compared to SMR. Principle of this strategy is a reforming reaction performed in an electrochemical way. From thermodynamic perspective, the introduction of a fuel such as methane lowers the open-circuit voltage, and thus the electricity consumption. Additionally, the reductive nature of methane diminishes the chemical potential difference between the anodic and cathodic compartments, further contributing to improved system performance. Compared with steam reforming reactors, the modular design of the electrolyser and the absence of extensive heat exchangers, allows this approach to be used to build small-scale hydrogen production units.

2.1.2 Biomass-based depolarised electrolysis

Biomass electrolysis presents a sustainable and energy-efficient alternative to conventional water electrolysis. Unlike water electrolysis, which requires high cell voltages (>1.8 V) and energy input (~4.8 kWh/Nm^3 H_2) [10], biomass electrolysis utilizes organic feedstock to generate hydrogen at significantly lower voltages (~0.6 V), reducing energy consumption by up to three times[11]. The energy balance of ethanol production—expressed as the energy return on energy invested (EROI)—varies significantly depending on the feedstock and production process. The most energy-efficient biofuel sources are the 1st generation ethanol, in particular that produced from sugarcane has a EROI ranging from 8:1 to 10:1.[12] The 2nd generation ethanol, derived from lignocellulosic biomass has an EROI ranging from 2:1 to 4:1[13] as it's a more complex and energy demanding process, but benefits from the utilisation of non-food biomass (e.g., agricultural residues, wood chips) and still offers a good carbon balance. Different biomass-derived feedstock offers distinct advantages in hydrogen production. Ethanol electrolysis requires relatively low input energy (1.6–2.3 kWh/Nm^3 H_2) and benefits from an established supply chain[14]. However, a big challenge is to find highly active catalysts for breaking the C–C bond to accomplish ethanol complete oxidation to CO_2 releasing 12 e^-. Moreover, in addition to CO_2, carbon-containing by-products (e.g. aldehydes) can be also produced. Glycerol, a by-product of biodiesel production, provides high hydrogen selectivity and valuable oxidation coproducts[15]. This process can be designed to co-produce value-added chemicals, significantly improving economic viability[16]. The most interesting feedstock is lignocellulosic biomass. It is an abundant and renewable hydrogen source. However, its complex polymeric structure, made of cellulose, hemicellulose, and lignin, requires pre-treatment to release fermentable sugars for electrolysis. This process is scalable for distributed hydrogen production, with an estimated H_2 cost of $2.50–$3.50/kg, making it competitive with clean hydrogen from electrolysis[17].

2.1.3 Enzyme mediated electrochemical processes

Enzyme-mediated electrochemical systems represent a biologically inspired and increasingly promising route for sustainable hydrogen production. These systems exploit hydrogenases - highly efficient metalloenzymes - as natural catalysts for the hydrogen evolution reaction.[18] Particularly, [FeFe]- and [NiFe]-hydrogenases have been integrated into electrochemical platforms to enable hydrogen generation under ambient conditions, providing an attractive alternative to platinum-based catalysis. Compared to platinum, enzyme-based systems demonstrate excellent catalytic behaviour, especially given their operation at low overpotentials and mild reaction environments.[17] Although platinum remains unmatched in universal catalytic performance, its scarcity and cost limit scalability. By contrast, enzymatic systems leverage earth-abundant materials and offer site-specific catalysis, making them attractive for clean hydrogen technologies.

In enzyme-electrode assemblies, hydrogenases are immobilized onto conductive supports such as carbon nanotubes, redox polymer matrices, or nanostructured metal oxides, enabling direct electron transfer.[18] Strategies to overcome oxygen sensitivity include protective encapsulation and protein engineering approaches to preserve catalytic activity under aerobic or semi-aerobic conditions.[19] Oxygen-tolerant [FeFe]-hydrogenases, such as CbA5H from *Clostridium beijerinckii*, can switch reversibly between an active oxidized state (Hox) and an oxygen-stable inactive state (Hinact).[20]

Structural studies used cryo-electron-microscopy for insights in the protein structure, further revealing a “safety cap” mechanism that protects the active site from oxygen damage.[21] Integration with nanostructured semiconductors has also advanced significantly. For instance, electrodes modified with TiO_2 nanostructures and immobilized [FeFe]-hydrogenase from *Clostridium perfringens* (CpHydA) achieved hydrogen production rates around 29 µmol $H_2 \cdot h^{-1}$, with a Faradaic efficiency exceeding 90%.[22]

In microbial electrolysis cells (MECs), hydrogenase-based bio-cathodes have achieved notable hydrogen production efficiencies. Albuquerque et al.[23] reviewed the progress in this field, reporting hydrogen yields up to 3.36 mol H_2/mol acetate under alkaline conditions (pH 11.2), operating at current densities up to 83.7 A/m^3.[24] In recent years, Webb and Milton[25] reviewed scalable electroenzymatic hydrogen production using engineered [FeFe]-hydrogenases on conductive electrodes, maintaining high Faradaic efficiencies. Additionally, Zhuang and Wang[26] updated the state-of the-art on enzyme-mimetic electrocatalysts based on hydrogenase active site architectures, with many examples achieving increased catalytic stability and rates.

2.1.4 Sea- and wastewater electrolysis

Utilization of non-pure sources of water such as seawater or brackish water, theoretically represent a financial and geographical solution for hydrogen production, as often the places where renewable energies are abundant, fresh water is scarce (e.g. north Africa and southern Europe). Though the financial feasibility of this is constantly discussed[27], as the economic cost of seawater desalination and purification, represents - over the overall H_2 production cost - less than 1% in most cases and less than 5% in the most extreme of cases.

The contaminants present in these water sources can result fatal for the current available technologies, with chlorine and sodium being both the prime example and the most abundant contaminant, causing, for example, the chlorine evolution reaction in PEMEL[28] and sodium poisoning the sulfonic groups of the membrane[29]. Nevertheless, continuous efforts are carried out for the development of materials that could adapt PEMEL and AEMEL to cope with non-pure water electrolysis[30] (e.g. complex and noble metal catalysts, electrolyte additives, electroactive substrates) as well as alternative routes to electrolyse seawater that avoid the issues that impede PEMEL or AEMEL utilization for example; Solid oxide seawater electrolysis[31], Molten Carbonate Electrolysis, Sulfion oxidation electrolysis [32] or self-damping electrode [33].

2.2 Photolytic hydrogen processes

2.2.1 Artificial photosynthesis, photocatalysis and photoelectrochemical cells

Photoelectrochemical (PEC) and photocatalytic (PC) solar technologies are recognized as long-term alternatives to coupled photovoltaic-electrolysis units. While the hydrogen production rate is lower than in high intensity electrolysis, PEC and PC systems are simple, bringing about additional options for abundant materials and sustainability. So far, low production rates have not been compensated by solar concentration technologies, as a fall in the solar to hydrogen (STH) efficiency typically occurs [34]. Active materials in PEC and PC systems combine light capture and catalytic abilities in a single component. The PEC cell allows separate compartments, one of them ideally generating pure H_2. On the contrary in a PC reactor, being the simplest configuration, H_2 evolves mixed together with the other reaction products. Therefore, implementation of PEC and PC concepts require specific research efforts, which have received attention from European programmes since FP7 and H2020 to the present.

As a result of SOLHYDROMICS project, a PEC prototype, achieved around 1% STH efficiency for 1-day operation [35]. A first scaling PEC design was accomplished during the ARTIPHYCTION project, consisting of 20 modules of 5 PEC-PV units with a 2% STH efficiency, 1000 h of operation and a total H_2 production of > 1 g/h [36]. Another relevant PEC scaling project was PECDEMO, with STH efficiency of 10%, stability of 1000 h and electrode areas of 50 cm^2.[37] After that, FotoH2 focused on abundant materials and the economic viability of the PEC prototype [38]. Other currently active projects consider the use of metal-free materials [39] or the simultaneous waste treatment with the synthesis of high added-value chemicals [40]. On the purely PC mechanism, a large-scale array of panel reactors was demonstrated by Domen et al.[41]. Current trends focus on novel materials [42] and waste treatment [43].

2.3 Biomass-based and thermochemical processes

2.3.1 Two-stage anaerobic digestion

Two-stage anaerobic digestion (TSAD) systems represent a promising route for decentralized biological hydrogen production using biomass feedstock. These systems, followed by a methanogenic stage, also enable energy-rich bio-hythane generation. Notable performance has been observed in a thermophilic two-stage continuous stirred tank reactor (CSTR) system, which co-digested livestock effluents with starchy wastes. The system achieved volumetric production rate of hydrogen of 2.1 Nm^3H_2/m^3d with a corresponding yield of 99 Nm^3H_2/kg_{vs} indicating strong energy recovery potential. In Bulgaria, a lab-scale pilot using corn steep liquor demonstrated hydrogen production rates of up to 1.0 L/L/day with H_2 concentrations near 35% [44]. Italian studies involving municipal organic waste and waste sludge under thermophilic conditions yielded 24 L H_2 and 570 L CH_4 per kg of volatile solids, underscoring the potential for urban-scale integration and fuel-grade bio-hythane recovery [45]. Náthia-Neves et al.[46] conducted a pilot-scale co-digestion study using restaurant food waste and vinasse, reporting hydrogen yields of up to 76.5% H_2 by volume after 8 days. These findings validate the operational efficiency of TSAD systems in managing diverse organic residues.

A techno-economic analysis by Mahmod et al.[47] on palm oil mill effluent estimated 225,225 m^3 of $BioH_2$ and 51.19 million m^3 of $BioCH_4$ per annum, with production profitability feasible at payback time of 8 years and internal rate of return of 21.48%. A more recent review outlines payback times between 2 and 6 years, also citing examples at TRL greater than or equal to 5, highlighting that TSAD favoured an energy recovery higher than 30% compared to the monostage AD [48]. This suggests that TSAD can be cost-effective, particularly when integrated into existing waste treatment infrastructures and utilizing readily available organic residues.

2.3.2 Thermochemical cycles and biomass-based processes

Thermochemical cycles produce hydrogen through a series of chemical reactions involving high-temperature heat, often sourced from concentrating solar energy. These cycles split water into hydrogen and oxygen without direct electrolysis, offering the potential for high-efficiency operation at scale. Ongoing research is focused on improving the durability and redox performance of active materials—typically metal oxides—while reducing the overall thermal input required. The ability to decouple reduction and oxidation steps also allows for integration with intermittent renewable sources and thermal energy storage, supporting continuous hydrogen production even in variable conditions. Thermo-electrochemical cycles working in solid-state are emerging as alternative processes to reduce operational temperatures up to 850 °C.

Plasma-assisted hydrogen production involves the generation of reactive environments using electric discharges to activate gas-phase reactions at lower bulk temperatures.

These systems are particularly relevant for the conversion of methane, ammonia, or other hydrogen carriers, and can operate with or without catalysts. Plasma reactors offer rapid response times, tuneable reaction pathways, and compact designs, making them suitable for modular or distributed applications. While still at relatively low technology readiness levels, advances in reactor engineering and process control are steadily improving their efficiency and scalability.

In the frame of hydrogen production from biomass through thermochemical processes, gasification and pyrolysis of lignocellulosic feedstock are the most common processes. However, their wide implementation is held back by several technical and economic challenges that should be addressed at both research and process integration levels. In fact, process integration can help reduce the cost of biomass thermochemical conversion by leveraging economies of scale, similar to those seen with more centralized feedstock such as petrol or natural gas. In particular, the integration of biomass-based thermochemical routes with other processes or streams of the clean hydrogen value chain or renewable energy and chemicals value chain can enhance overall efficiency and sustainability [49,50].

Regarding the type of biomass employed, the use of lignocellulosic biomasses is well established. However, in the view of circular economy other biomasses with high humidity degree coming from different processes may be used. On the other hand, a key limitation in current thermochemical processes is the utilization of air and nitrogen (in gasification and pyrolysis, respectively), which leads to diluted hydrogen streams. The production of higher quality hydrogen can be addressed operating on the process by reducing the nitrogen input using for instance enriched air or oxygen [51] coming from other processes or utilizing efficient separation systems, such as pressure swing adsorption (PSA) or membrane systems, suitable for the small scales typical of decentralized biomass facilities.

Biomass pressurized pyrolysis is an advanced thermochemical conversion technique for producing hydrogen, which aligns with current sustainability and decarbonisation strategies [52,53]. This process entails the thermal degradation of biomass feedstock under elevated pressures (typically 5–50 bar) and high temperatures (450–650 °C) in an oxygen-free environment, yielding syngas composed predominantly of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and minor hydrocarbons.

Operating under pressurized conditions has demonstrated increased efficiency in hydrogen production and improved syngas quality compared to atmospheric pyrolysis processes. High pressures enhance hydrogen yields by promoting reforming reactions and suppressing tar formation, thus generating a cleaner syngas stream suitable for subsequent hydrogen extraction and purification stages [54]. Additionally, the integration of catalytic systems within the pyrolysis reactor can significantly enhance hydrogen selectivity, reduce undesirable by-product formation, and lower energy requirements [55]. The adoption of biomass pressurized pyrolysis for hydrogen production provides several technical advantages, such as increased energy density, higher purity of the syngas produced, and improved compatibility with existing hydrogen infrastructures, facilitating downstream applications like fuel cells and industrial processes [56]. Moreover, the utilization of biomass as a renewable feedstock contributes to waste valorisation, supports circular economy principles, and enhances regional energy security through local resource exploitation [53].

Nevertheless, significant technical challenges persist, notably the optimization of reactor configurations, selection and stability of catalysts under harsh operational conditions, and process cost reductions to ensure economic viability. Overcoming these challenges demands ongoing research, innovation, and supportive policy frameworks to encourage industrial-scale deployment.

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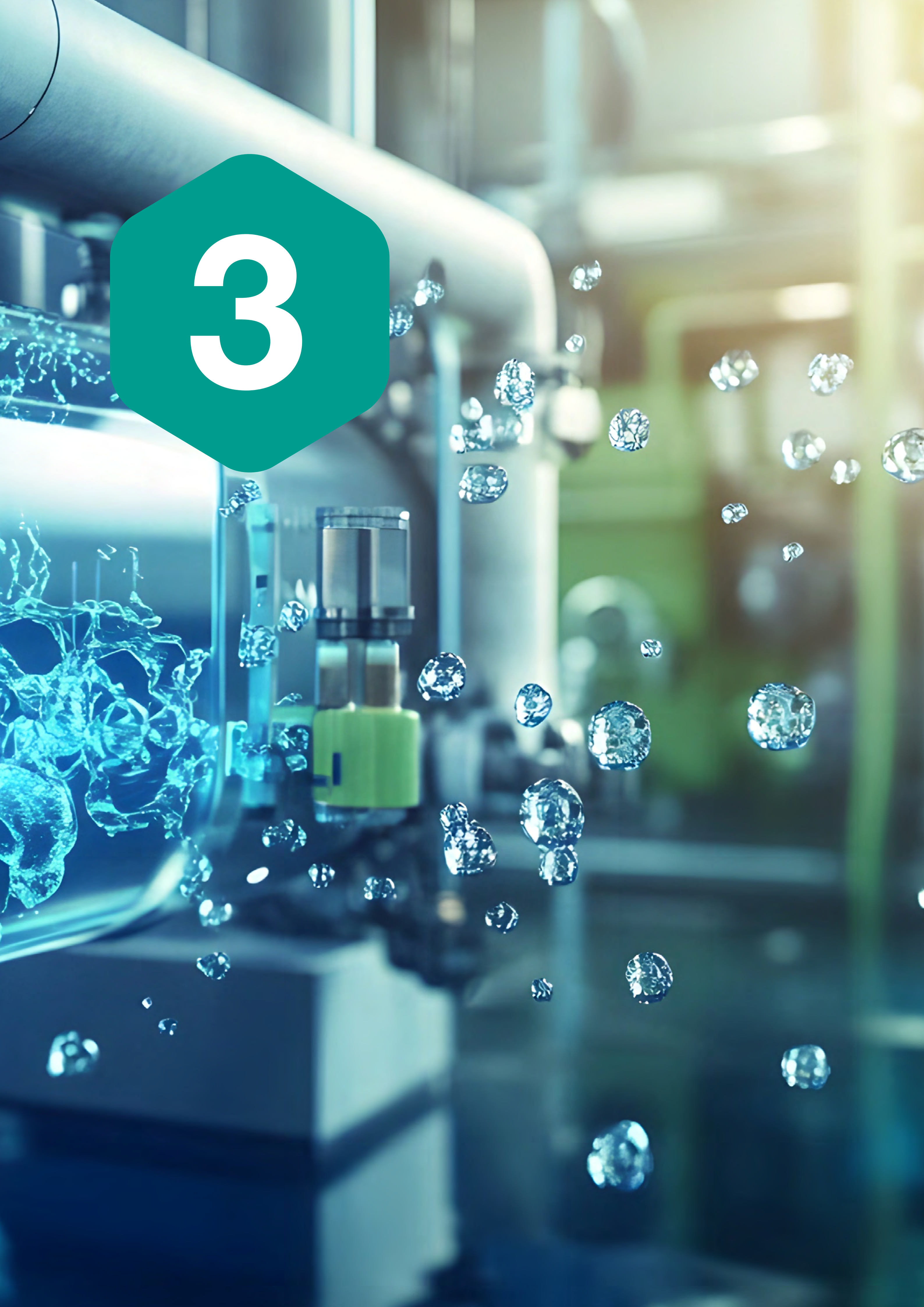

Research challenges

3.1 Electrochemical processes challenges

As previously mentioned in the section 2, compound-based depolarized electrolysis introduces compounds to alter the oxidation (anodic) reaction on an electrochemical cell. By replacing the OER for a less energy demanding reaction, the overall cell voltage is lowered and an extra anodic product is obtained, ideally more valuable than the O_2 produced by the OER. This approach helps mitigate the overall costs of the process, reducing the production cost of the obtained H_2. One of the advantages of the SDE is the cross-compatibility of its components with water electrolysis as well as fuel cells, nevertheless it also represents an opportunity to further develop these technologies. To the date, no specific component has been designed or manufactured, therefore the whole electrochemical cell and its components (gas diffusion layer (GDL), catalyst coated membranes (CCMs), Flow field and Gaskets) have potential to be improved. To achieve long term durability and stability, considering the challenges regarding the feedstock and products – with e.g. SO_2 and H_2SO_4 being highly corrosive and reactive – research and studies must be carried out to determine the effect of each component over and its relation to SDE performance (viscosity, flow velocity, porosity, membrane lifetime, F- emissions, water retention, etc.). Current SoA does not surpass 100 hours of operation and still, variable operation, contaminants in the SO_2 feed as well as the reaction mechanisms, are yet to be studied.

To optimize efficiency of biomass based electrochemical processes, various electrocatalysts have been investigated, including Ni-based catalysts, which improve biomass oxidation at the anode. Recently, polyoxometalates (POMs) have emerged as promising electrocatalysts due to their high redox activity, tuneable electronic structure, and ability to facilitate multi-electron transfer reactions. POMs have shown potential in improving catalytic efficiency for both HER and OER, thereby enhancing overall hydrogen production efficiency from biomass-derived feedstock. Specifically, POMs, such as phosphomolybdates and phosphotungstates, function as electron shuttles, facilitating oxidation reactions and improving catalyst stability under acidic and alkaline conditions [57]. These materials also enable selective oxidation of biomass-derived molecules, increasing the yield of value-added products like FDCA and glyceric acid. Another promising approach involves the use of $FeCl_3$ as a redox mediator in biomass electrolysis. $FeCl_3$ can effectively facilitate electron transfer in oxidation reactions, improving the efficiency of lignocellulosic biomass breakdown. Studies have shown that $FeCl_3$-assisted electrolysis can lower the overpotential required for oxidation, reducing energy consumption and increasing hydrogen selectivity [58]. This approach is particularly useful in combination with Ni- or POM-based catalysts, creating synergistic effects that boost overall process efficiency.

3.2 Photolytic hydrogen processes challenges

The process that is typically considered as an inspiration, natural photosynthesis, is not particularly efficient or fast in terms of solar energy conversion. Artificial photoactivated processes apparently require a high solar-to-hydrogen (STH) efficiency to balance fabrication and operation costs. Research on low cost, abundant non-critical materials for all cell/ reactor components is still timely, also including polymeric, organic, hybrid and biological materials, as well as their chemical stability for long life under prolonged solar irradiation.

Recently, ideas for the use of non-pure water, simultaneous wastewater treatment and oxidative photo-reforming towards high added-value products have been considered in various EU projects. However, they will probably require further efforts for their intrinsic complexity and multiplicity of possible target chemicals. Finally, combining photolytic methods with other physical/chemical aids has been proposed, but still remains a powerful source of new approaches.

Photoactivated hydrogen production systems that utilize hydrogenases continue to advance as promising routes for sustainable hydrogen fuel generation. A major development in semiconductor-enzyme integration is the use of TiO_2 nanoparticles as photoanodes. In a study by Polliotto et al.[59], highly active [FeFe]-hydrogenase enzymes from *C. perfringens* were anchored onto modified TiO_2 surfaces (N-TiO_2, more efficient than bare TiO_2 in harvesting visible light, bypassing the limitation of expensive dye-sensitizing with Ru-based systems). Tested for hydrogen production under direct solar light with triethanolamine (TEOA) as a sacrificial donor, these systems showed turnover frequency numbers (TOF) of $4.1 \pm 0.1\ s^{-1}$.

Engineering photosynthetic organisms for integrated hydrogen production is another active area of research. For example, fusion of Hydrogenases with Photosystem I – a specific type of protein-pigment complex – in genetically engineered cyanobacteria and algae, facilitate direct electron transfer from light-harvesting complexes to hydrogenase enzymes [60].

As for artificial photosynthesis, Reisner group reported in 2018 a semi-artificial system for the unassisted, light-driven water splitting with PSII and [FeFe] hydrogenase, able to generate H_2 and O_2 from water with high Faradaic efficiencies in a 2:1 ratio and proposing an effective strategy to stabilize biotic–abiotic hybrid systems [61].

PH2OTOGEN [43] project focuses on optimizing transparent, porous, conductive photocatalyst supports that electronically couple hydrogen-evolving and oxidizing particles. The goal is to achieve a solar-to-hydrogen efficiency exceeding 5% over 500 hours of operation in a 500 cm^2 demonstrator.

The PHOTOSINT [62] project aims to develop sustainable processes for producing hydrogen and methanol using only sunlight, wastewater, and CO_2 as inputs. This involves the creation of new catalytic materials and the integration of perovskite solar photovoltaic cells with photoelectrochemical systems to enhance efficiency. The project seeks to maximize solar-to-fuel conversion rates and assess the feasibility of scaling up these renewable energy technologies for industrial applications.

3.3 Thermochemical cycles and biomass-based processes challenges

Regarding biomass-based processes, enhanced process control was a central theme in recent TSAD research. Furthermore, the impact of reactor temperature and hydraulic retention time (HRT) on microbial activity was reiterated across multiple case studies. In parallel, microbial community studying and engineering has emerged as a critical component for process stability [63-65].

Several pilot studies emphasized the potential of underutilized and co-digested biomass streams. Using cacao pod husk (CPH) as a feedstock, Kriswantoro et al.[66] reported successful biohydrogen production. This demonstrated the feasibility of agricultural waste valorisation in a TSAD system. TSAD is also increasingly being positioned within integrated municipal and industrial waste management strategies. Dell'Orto and Trois [67] evaluated the integration of TSAD into South African municipal solid waste frameworks, demonstrating its potential to reduce methane emissions and divert organics from landfills. Masoud et al.[68] reported high hydrogen production on bio-char derived from sugarcane bagasse and then employed as a conductive material in two-phase AD of food waste.

The integration of biomass thermochemical conversion with other processes of the hydrogen value chain can make these processes more suitable for the industrial application of hydrogen production. In this framework the utilization of biomasses from different sources and the reduction of the inert gas content can be ways to increase the competitiveness of gasification. However, these solutions need the development of innovative materials while pursuing process integration. In fact, the utilization of biomasses with high degrees of humidity or of impurities may change the gas composition at the thermochemical process outlet not only in terms of water but also in terms of poisonous impurities. This has an important effect on the downstream catalytic upgrade, needed to reduce the amount of hydrocarbons, tars and impurities, increasing the hydrogen content while preserving the catalyst stability. In this framework the development of stable and critical raw material (CRM)-Free catalysts, including biocatalysts, still need to be addressed at low-TRL to get insights into the mechanism and reaction conditions that can lead to deactivation and to catalytic formulations with high stability and activity.

Regarding the reduction of inert gas in the outlet gas (e.g. using enriched air in gasification) by increasing the amount of oxidant may lead to temperature changes in the gasifier and in the upgrading process. In this framework innovative materials able to resist and disperse heat in a more efficient way, while retaining performances and catalytic stability are necessary. The use of membranes has shown promising results, though the presence of impurities in the gas produced from biomasses may alter their stability and performances. For this reason, innovative systems also based on disruptive concepts for hydrogen separation on small-medium scale should be developed.

Importantly, microwave-assisted thermochemical water splitting has demonstrated the ability to lower the reduction temperature of redox-active materials such as lanthanum-doped ceria to below 500 °C. This reduction in temperature requirements decreases the thermal burden of the process and enhances compatibility with lower-grade heat or renewable electricity sources. Overall, these alternative production routes are contributing to a broader technological landscape in which hydrogen can be generated through multiple energy vectors—thermal, electrical, or hybrid—depending on local resources and infrastructure. As these systems advance toward higher technology readiness levels, emphasis will be placed on system integration, process modelling, and techno-economic validation. Their development supports the goal of creating a flexible, resilient, and decarbonized hydrogen supply chain that complements large-scale electrolysis and other established technologies.

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Research Priorities for the Future

Despite the growing interest in a hydrogen economy, virtually all alternatives for achieving depolarized electrolysis remain under- (or non-) explored. The overwhelming focus of research and funding has been directed toward the most popular technologies (PEMEL, AEL and AEMEL). However, there are several cases where alternative electrolysis pathways, like depolarized electrolysis, could serve as complementary solutions especially in contexts where PEMEL or AEMEL systems are not feasible or cost-effective. For these alternatives to become competitive, a thorough understanding of the electrochemical reaction mechanisms is essential. This knowledge would enable the development of specialized components tailored to optimize system performance. Currently, no commercial components are specifically designed for any type of depolarized electrolysis. As a result, research and development in this area have relied on modified components originally intended for PEMEL, AEMEL, or fuel cells. It would not be far-fetched to estimate that, with targeted component development and a deeper understanding of the respective system's reaction dynamics, these alternative technologies could emerge as a competitive solution for industrial-scale hydrogen and clean chemical production in the near future.

Techno-economic analyses suggest that ethanol and glycerol electrolysis are currently the most cost-competitive, while lignocellulosic biomass and waste electrolysis offer long-term scalability for net-zero carbon hydrogen production. Life cycle assessments indicate that biomass electrolysis can reduce CO_2 emissions by up to 86% compared to steam methane reforming (SMR) [10]. Biomass waste electrolysis provides an alternative for reducing emissions from bio refinery processing. Despite its potential, biomass electrolysis faces challenges, and further research is required to improve feedstock processing and scale up this technology for industrial deployment. Future research should focus on improving reaction selectivity, enhancing electrolysis cell efficiency, and developing scalable bio refinery-integrated hydrogen production systems. By addressing these challenges, biomass electrolysis could play a crucial role in the future hydrogen economy while contributing to environmental sustainability.

Photocatalytic (PC) and photoelectrochemical (PEC) systems for H_2 production need design concepts demonstrating economic viability. A way towards efficient and economic artificial photosynthesis preferably lays on supported photocatalysts, facilitating reutilization, and bias-free PEC systems, producing separate pure H_2 and totally avoiding electricity consumption. New resources for solar light management, including light concentration, are yet to be investigated, trying to keep the maximum STH efficiency. Widening the wavelength range of captured and transformed solar photons, keeping a high quantum efficiency, will also improve the STH conversion. Scaling cell/reactor configurations require suitable combinations of optical characteristics of absorption, transmittance, etc. in active composite materials and stacked layers. In addition, connection to H_2 collection and compression systems, as well as direct local uses of the produced H_2 are yet to be researched as well.

Results on pilot systems underline the feasibility, scalability and adaptability of two-stage fermentation platforms for sustainable hydrogen production, particularly when integrated with circular bio-economy frameworks and waste management strategies. Detailed studies on optimised microbial consortia are required in order to obtain inoculum which is resilient to inhibitory compounds and effective in processing possible recalcitrant biomasses such as lignocellulosic (from corn stover, wheat straw and rice husk) or chitin, feathers and keratin-rich waste (e.g., poultry processing residues) or food processing waste (for example from orange and olive) with high content of inhibitory compounds like phenolics, tannins and terpenes. While specific cost assessments of hydrogen produced via two-stage anaerobic digestion are still emerging, available studies suggest promising economic feasibility under certain conditions.

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Concluding remarks

There are multiple approaches to produce hydrogen through alternative pathways that are noteworthy and may provide solutions to more specific applications and use case scenarios. However, these approaches at the moment lack support, as they still require substantial efforts to both develop the technologies as well as to understand some of the underlying fundamental mechanisms, sensitivities and limitations. Further development of these alternative hydrogen production technologies is essential to address a critical, yet often overlooked, gap in the transition toward truly sustainable production systems, meaning the possibility to provide a clean, sustainable and economical solution for all the scenarios where energy, fuel, or storage is needed, status that currently can't be fully covered by just PEMEL and AEL technologies. Achieving true sustainability requires solutions that can operate across the full spectrum of energy, manufacturing, and industrial scenarios, many of which cannot be addressed by existing mainstream technologies due to technical, economic, or logistical constraints. The technologies presented in this report offer a diverse set of complementary solutions, each contributing in its own way to the establishment of a robust hydrogen ecosystem;

- **Depolarized Electrolysis** capitalizes industrial chemical waste—such as SO_2, and NO_x—as a feedstock, enabling the co-production of clean hydrogen and value-added chemicals, while promoting circularity in heavy industries.
- **Biomass-Based Processes** offer cost-effective pathways for converting municipal and biological waste into hydrogen, creating opportunities for integrated value chains that support the transition to a zero-waste society.
- **Photolytic Processes** enable passive energy storage in the form of hydrogen by mimicking natural processes such as photosynthesis, representing a novel approach to solar-to-fuel conversion.
- **Thermal Processes** can capitalize on otherwise unused waste heat, improving overall energy efficiency and resource utilization.

Overall, these alternative production routes collectively contribute to a broader technological landscape in which hydrogen can be generated through multiple energy vectors—thermal, electrical, or hybrid—depending on local resources and infrastructure, allowing the technology to adapt to diverse contexts and supporting the development of a flexible, inclusive, and sustainable hydrogen economy. Under the right conditions, covered throughout this report, these technologies present the potential to produce economically competitive H_2 in the future. As these systems advance toward higher technology readiness levels, emphasis should be placed on further understanding and development of these technologies, system integration, process modelling, and techno-economic validation. Their development supports the goal of creating a flexible, resilient, and decarbonized hydrogen economy that complements and coexists with large-scale electrolysis and other established technologies.

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