

Review

Addressing Environmental Challenges: The Role of Hydrogen Technologies in a Sustainable Future

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Abstract: Energy and environmental issues are of great importance in the present era. The transition to renewable energy sources necessitates technological, political, and behavioral transformations. Hydrogen is a promising solution, and many countries are investing in the hydrogen economy. Global demand for hydrogen is expected to reach 120 million tonnes by 2024. The incorporation of hydrogen for efficient energy transport and storage and its integration into the transport sector are crucial measures. However, to fully develop a hydrogen-based economy, the sustainability and safety of hydrogen in all its applications must be ensured. This work describes and compares different technologies for hydrogen production, storage, and utilization (especially in fuel cell applications), with focus on the research activities under study at SaRAH group of the University of Naples Federico II. More precisely, the focus is on the production of hydrogen from bio-alcohols and its storage in formate solutions produced from renewable sources such as biomass or carbon dioxide. In addition, the use of materials inspired by nature, including biowaste, as feedstock to produce porous electrodes for fuel cell applications is presented. We hope that this review can be useful to stimulate more focused and fruitful research in this area and that it can open new avenues for the development of sustainable hydrogen technologies.

Keywords: hydrogen; production; bio-alcohol; storage; formic acid/formate; fuel cell; biowaste



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1. Introduction

Population growth as well as industrialization have been accompanied by a huge increase in energy consumption, causing severe environmental impact in terms of fossil fuel depletion, pollution, and increased content of greenhouse gases [1]. Figure 1 shows the trend of the global warming and reports temperature and cumulative CO₂ emissions until 2050. The grey range with its central black line draws a corresponding estimate of the human-caused share of historical warming. Coloured areas show the global surface temperature projections, and thick coloured central lines show the median estimate as a function of cumulative CO₂ emissions for different scenarios, ranging from very low (SSP1-1.9), low (SSP1-2.6), intermediate (SSP2-4.5), high (SSP3-7.0), to very high (SSP5-8.5) [2].

To limit human-caused global warming to a specific level, we need to restrain the cumulative CO₂ emissions, reaching net zero or net negative CO₂ emissions, along with reductions of other GHG emissions. To this end in the Paris Agreement countries agreed to reach the following targets: a reduction of 50–52% of CO₂ emissions by 2030; carbon pollution-free electricity by 2035; net ZERO GHG emissions by 2050 [3]. In Figure 2, the required CO₂ trend emissions is shown as function of time.

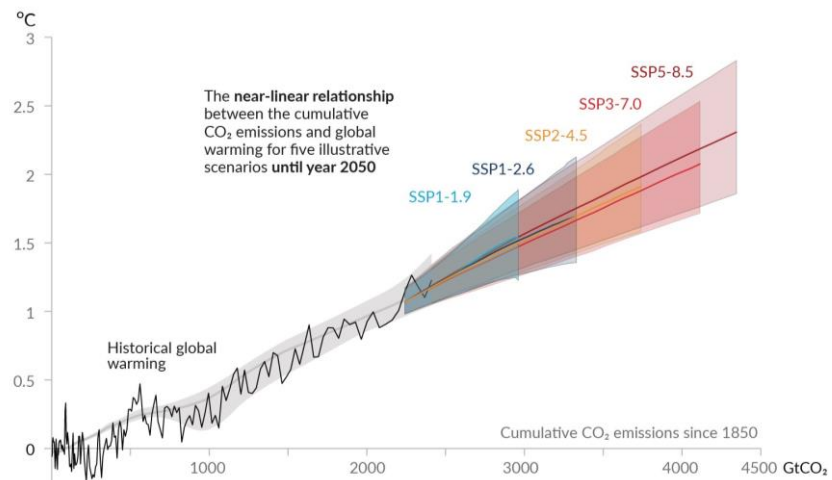


Figure 1. Global surface warming as function of cumulative CO₂ emissions until 2050 [2].

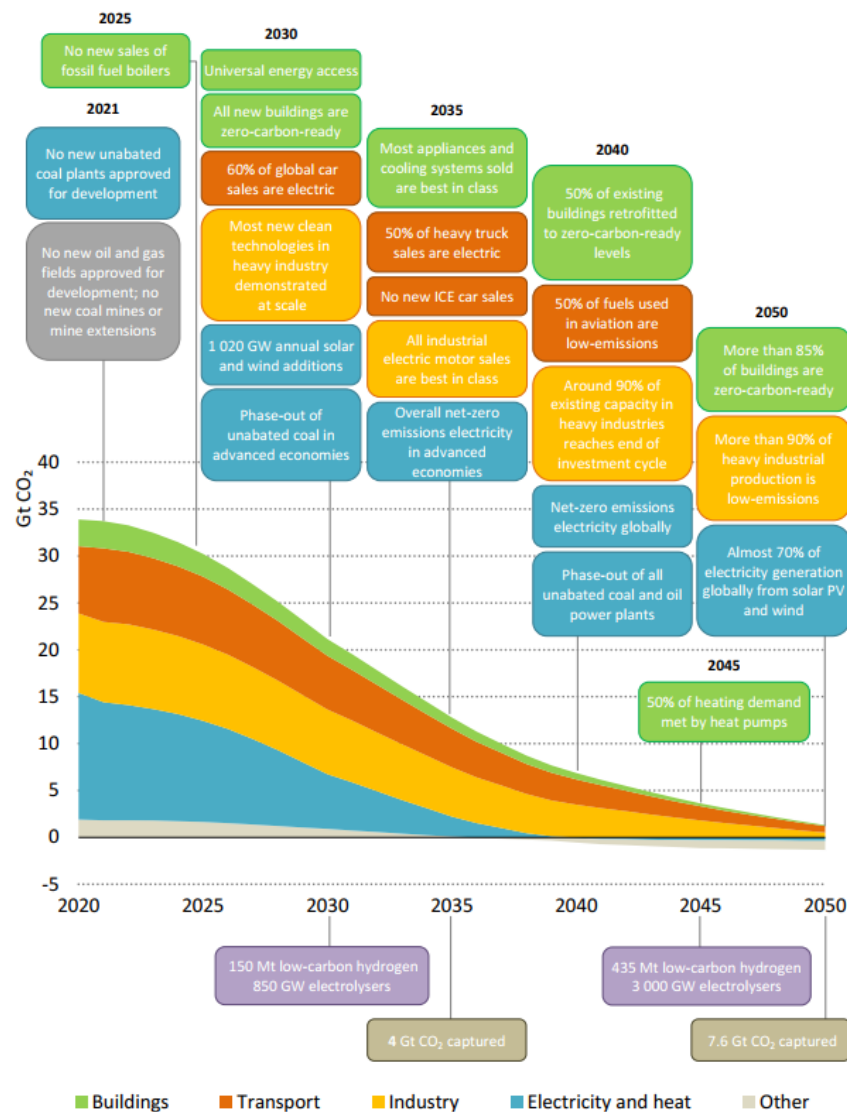


Figure 2. Global economy-wide net greenhouse gas emissions. A net-zero system will require transformative technologies to be deployed across sectors [3].

To reach these goals, a complete energetic transition towards renewable, cleaner, and more sustainable sources is required, with the most important strategy being the develop-

ment of H₂ technologies and their widespread use in human activities. H₂ is intrinsically clean since it only produces water, thus contributing to decarbonization. H₂ can be produced by different means, including renewable sources. It releases a significant amount of heat when burned without pollution. Furthermore, it can be exploited in a huge range of applications, replacing traditional fossil fuels and including the transport, heat, industry, and electricity sectors [4]. Finally, because of the plethora of production technologies, its availability is not affected by outside influences [5]. Despite the significant technological potential and the possibility of transitioning to a low-carbon economy, hydrogen as an energy carrier remains limited, with only 6% of H₂ production being used for this purpose. Most of the hydrogen is instead used as an intermediate in industrial chemical production, emphasizing its constrained role in meeting global energy demands [6].

To reach the goal of widespread use of H₂, all the related technologies must be developed and optimized to meet sustainable targets. Figure 3 shows the H₂ cycle, evidencing that it is based on four cornerstones: production, storage, transportation, and use. Each step must be managed to eventually produce clean energy; H₂ must be produced, and then the first action is the optimization of H₂ production unit. Produced H₂ must be stored and transported in a green, sustainable, and safe way. Finally, H₂ should be used for clean and efficient energy production through high-performance devices that ensure significant energy conversion rates by using fuel cells.

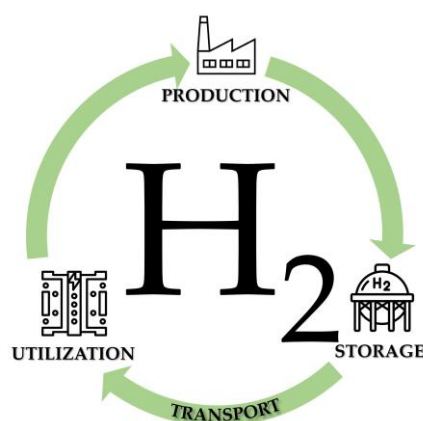


Figure 3. The H₂ cycle.

In this context, this review discusses the most recent advances in each operation of the H₂ cycle, dealing with the studies that concur with the development of sustainable technologies for H₂ production, storage, and use.

In each section of the work, the technologies under study in the SaRAH (Safety, Risk Analysis and Hydrogen) group of the University of Naples Federico II [7] are described, reviewed, and discussed. According to the authors, these are the most promising technologies in the H₂ cycle available in the literature.

In the first part of the review, the potential use of biowaste-derived alcohols for carbon-neutral H₂ production is presented. Bio-alcohols can be produced directly from renewable biomass; therefore, they stand as a sustainable resource. Reactions, operating conditions, main catalysts, and comparison of literature results are described for each production method.

The second part of the review discusses both traditional and innovative methods for H₂ storage, with a focus on the recent attention given to formates, the salts of formic acid (FA), as a sustainable alternative to conventional approaches. Indeed, FA can be derived from CO₂ or lignocellulosic biomass; thus, it serves as a renewable source for high-purity hydrogen synthesis and catalytic transfer hydrogenation (CTH) reactions.

Overall, significant reductions in CO₂ emissions could result from the use of bioderived compounds, such as lignocellulosic biomass, as starting materials for H₂ production and storage.

In the third part of the review, H₂ use has been explored within fuel cell technologies. Attention is paid to these devices since they allow for an efficient conversion of chemical

energy into electrical energy. Therefore, we describe the types of fuel cells working with H₂. Moreover, the performances of H₂ fuel cells have been compared with those of other energy conversion systems, and the challenges related to fuel cell full exploitation have been examined. In this regard, nature-inspired materials, such as biowaste, have been described as intriguing and promising templates to create porous electrodes, thanks to their intricate porous structures, impressive mechanical and thermal stability, widespread availability, and cost-effectiveness. Notably, novel technologies such as electrospinning and spin coating have been examined for their conversion of biowastes into high-performance photo-electrocatalysts for fuel cells.

2. Hydrogen Production from Bio-Alcohols: Focus on Bioethanol

Biowaste-derived alcohols represent an important alternative feedstock for carbon-neutral hydrogen production. Since they can be produced directly from renewable biomass, they have a sustainable feature [8]. CO₂ emissions from producing hydrogen using bioderived sources are offset by the CO₂ previously absorbed by these sources, resulting in net zero CO₂ emissions [9].

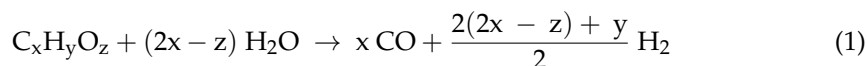
Bioethanol is traditionally made from plant by-products such as sugarcane, corn, and wheat (first-generation). However, lignocellulosic (second-generation) and algal biomass (third-generation) are now explored due to food sustainability concerns [10]. However, second-generation raw materials necessitate further procedures, including pre-treating lignocellulose, to generate fermentable substances. The challenge remains in maintaining the cost-effectiveness of these processes. Additionally, research in the third-generation sector is still in its early stages due to limited investment and design hurdles [11]. Annual production of bioethanol is steadily increasing, with a projected global output and consumption of nearly 134.5 billion liters by 2024. The cost of raw materials has a significant influence on bioethanol production expenses, accounting for between 40 and 75% of the total cost [12]. At current pricing, the anticipated cost of advanced bioethanol is between USD 1.04 and USD 1.45 per liter of gasoline equivalent (LGE) [13]. Minimising greenhouse gas emissions, ensuring energy security, and promoting agricultural practices in rural areas are all measures that can assist in offsetting the production of bioethanol.

Researchers have investigated a variety of methods to manufacture hydrogen from light alcohols, such as steam reforming (SR), partial oxidation (PO_x), autothermal reforming (ATR), photocatalysis (PC), and electrocatalysis (EC). In the following sections, these methods are discussed in detail, and the hydrogen production process under study by the SaRAH group is presented.

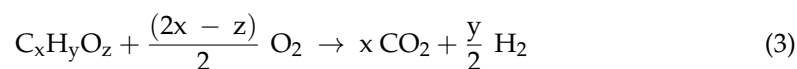
2.1. Reforming

Steam reforming (SR) is a highly advanced technique used in the petrochemical industry to convert natural gas, primarily methane, into hydrogen. However, it results in 8–13 Kg CO₂eq/KgH₂ emissions, both as a product reaction and for heating the reactor due to the reaction endothermicity [14]. Today, the research aims to expand the capabilities and adaptability of SR technology beyond its dependence on natural gas. One approach involves investigating alternative reactants, such as oxygenated hydrocarbons such as methanol [15–17], ethanol [15,18–20], glycerol [21,22], dimethyl ether, acetone, and acetic acid, as well as heavier hydrocarbons ranging from C₃ to C₁₀ [23].

For oxygenated hydrocarbons, the stoichiometric SR reaction (1) is as follows: The CO can be further transformed to produce additional hydrogen and carbon dioxide through the exothermic water-gas shift (WGS) reaction (2).

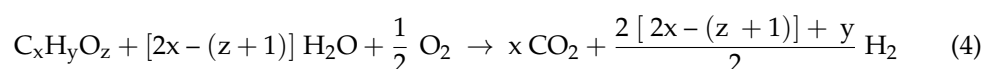


Another reforming technology is partial oxidation (PO_x) (3), in which partial combustion of the fuel produces hydrogen.



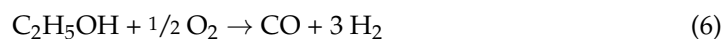
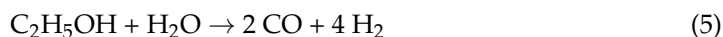
During PO_x, the fuel reacts with a limited supply of air or pure oxygen. The exothermic nature of the reaction means that it releases heat, avoiding the need for external heating. It is important to control the amount of air or oxygen supplied during partial oxidation to achieve the desired products and avoid complete oxidation, which would result in a reduced amount of hydrogen produced [24].

Autothermal reforming (ATR) (4) is a combination of both partial oxidation (exothermic) and steam reforming processes (endothermic) to supply the required heat and enable self-sustained reforming.



Fuel is first oxidized to heat up the reactor and then reacts with steam to produce hydrogen-rich syngas [25]. ATR has the potential to achieve high hydrogen yield and hydrogen selectivity because syngas can be produced from air or H₂O. By using the PO_x to produce heat and the SR to increase hydrogen production, the ATR technique produces a thermally neutral process [26].

In the case of ethanol, ethanol SR (ESR), PO_x, and ATR reactions are reported in the following (5)–(7) and are accompanied by the water-gas shift reaction (WGS) (2) to produce hydrogen:



In Table 1 are reported the operating conditions (temperature, pressure, feed ratio) of the ethanol reforming technologies.

The reaction pathway of ESR has been extensively studied, and the mechanism complexity is widely reported [27–29] since different parallel reactions occur simultaneously with hydrogen production. The product distribution depends on both the nature of the catalyst (i.e., active sites, support, precursor, preparation methods) and the reaction conditions, e.g., temperature, water/ethanol ratio, and feed flow rate. The complex set of by-products includes carbon monoxide (CO), methane (CH₄), ethane (C₂H₆), ethylene (C₂H₄), and acetaldehyde (CH₃CHO) [30].

Supported metal catalysts are commonly employed for ethanol steam reforming (ESR), in which the support plays a crucial role in activating steam to produce oxygen. Oxygen stabilizes the metal particles present in the catalyst and promotes the gasification of coke, while the metal phases break the hydrocarbon bonds [8]. Non-noble metal-based catalysts are widely employed for ethanol reforming due to their relatively low cost and good activity for C–C and C–H bond cleavage [31]. Among Ni, Co, Fe, and Cu species, the highest activity and selectivity for hydrogen and the lowest formation of CH₄ are achieved by Co [32,33]. Noble metal-based catalysts (Pt, Pd, Rh, and Ru) have high activity and stability in ESR, but the resource scarcity and relatively high costs represent an obstacle for their large-scale application. In general, Rh-based catalysts emerge as the most active and selective for H₂ production, even at low temperatures [34–36]. The reaction is highly influenced by the kind of support: basic solids encourage the dehydrogenation to acetaldehyde, while acidic ones cause the dehydration to ethylene, a key precursor to coke in ESR [37]. The most investigated and widely adopted support is Al₂O₃, but due to its acidic nature, it induces coke formation. The selectivity of H₂ for Co-based catalysts decreased in the following

order: Co/Al₂O₃ > Co/ZrO₂ > Co/MgO > Co/SiO₂ > Co/C [38], while the higher activity and hydrogen yield are achieved by Co/ZrO₂ [39]. The Rh/Al₂O₃ catalyst showed the highest selectivity for H₂, while Rh/CeO₂-ZrO₂ exhibited the highest yield in H₂ [40].

For the ethanol PO_x, Salge et al. [41] reported that the H₂ yield increases in the order Rh-Ru > Rh > Pd > Pt for an alumina-supported catalyst and that Rh/CeO₂ appears as the most stable catalyst with a H₂ selectivity, thanks to the promotion of WGS and the limitation of ethanol dehydration by ceria [42].

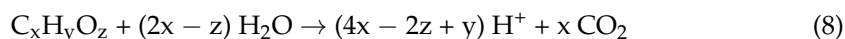
Also, in the case of ethanol ATR, Youn et al. [43] showed that nickel catalysts supported by the basic supports, ZrO₂ and TiO₂, had improved catalytic performance (hydrogen yield) and resistance to coke formation. Moreover, Gutierrez et al. [44] demonstrated that the Rh-containing catalysts are more suitable than the commercial Ni/Al₂O₃ catalysts for the ATR of ethanol.

Table 1. Operating conditions (temperature, pressure, feed ratio) of the ethanol reforming technologies for hydrogen production.

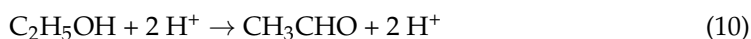
Technology	Temperature	Pressure	Feed Ratio	Ref.
Steam Reforming	450–650 °C	2–25 bar	Water/Ethanol = 3–6	[8,23]
Partial Oxidation	200–400 °C	1–10 bar	Air/Ethanol = 4	[42,45]
Autothermal Reforming	600–900 °C	1–10 bar	Ethanol/Air/Water = 1/0.3–0.5/2–3	[42,46]

2.2. Photocatalysis

Photo-assisted hydrogen production processes, a promising way to utilize solar energy and water or other renewable feedstocks, have received significant attention over the last few years [47]. Photocatalysis is a process in which light is absorbed by a semiconducting material to generate electron-hole pairs. When the energy of the irradiated light photon is greater than the band-gap energy of the semiconductor, the electrons migrate to the conduction band (CB) with positive holes left on the valence band (VB). Holes can oxidize either water or organic/inorganic compounds and split them into H⁺ protons on VB; electrons reduce the H⁺ species to produce H₂ on CB (Figure 4). However, the charge carrier reaction with the target substance competes with the recombination of an electron and a hole [48,49]. If bio-available oxygenated compounds are employed as sacrificial agents, this approach can be seen as nearly carbon-neutral since the CO₂ generated can be transformed back into biomass via plant photosynthesis [49,50]. A variety of organic compounds have been investigated, such as methanol [51,52], ethanol [53], glycerol [54,55], and raw biomass [56]. Compared to pure water splitting, the lower Gibbs free energy change leads to more efficient hydrogen production [57], and the formation of CO₂ as the product of the oxidation half reaction instead of O₂ decreases the recombination reaction [58]. The fundamental reactions are reported in (8)–(9) and in Figure 4.



For ethanol photoreforming, several mechanisms [57] were proposed. Among those, the most reliable considers the direct oxidation by photoexcited holes in acetaldehyde (10) and the simultaneous reduction of the H⁺ to H₂ (9). The acetaldehyde is then converted to CH₄ and CO. Through the WSR reaction (7), CO and CH₄ produce CO₂ and other H₂ [59–61].



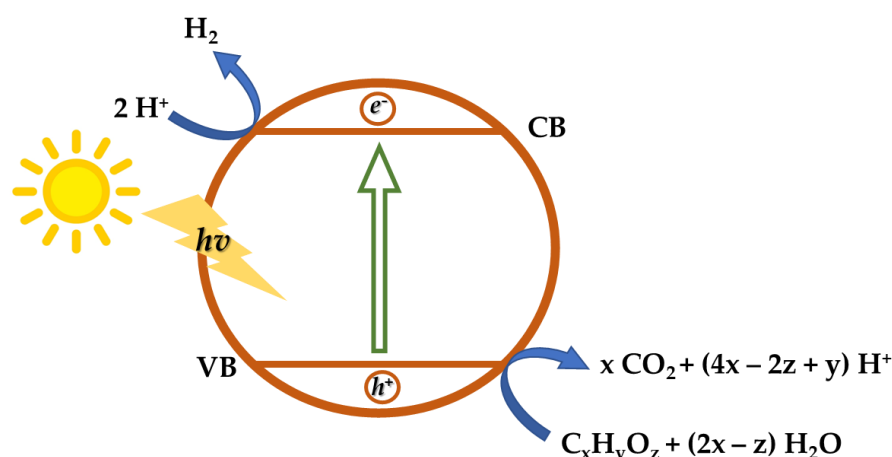


Figure 4. Schematic representation of the photocatalytic process of bio-alcohols and oxygenated hydrocarbons.

TiO₂-based photocatalysts have received the most attention among all photocatalysts, largely because of their favored characteristics, including an energy band location that can drive a variety of redox processes and, more importantly, H⁺ reduction, good chemical stability, and low toxicity [62]. However, the low efficiency for hydrogen production is due to fast electron-hole recombination in the bulk or on the surface of semiconductor particles. A promising approach to avoiding that is the deposition of metal nanoparticles on the surface of a photocatalyst that tend to take the electron and avoids recombination [63]. Noble metals including Au, Pd, and Pt are preferred for this purpose, even though Cu species have been proposed as a more economic choice [64–67]. Other key factors that influence hydrogen production are solution pH, alcohol concentration, temperature, and catalyst load [68]. Increasing the alcohol concentration initially increases the rate, but excessive amounts hinder water adsorption and decrease photocatalytic activity. The same rate trend occurs in relation to the catalyst load: at low catalyst loads, photon adsorption is not complete, while high catalyst loads lead to non-uniform adsorption of light photons. The solution pH affects the reaction rate due to the agglomeration of photocatalyst particles and to variation of the surface charge, which influence the absorption of H⁺ and alcohols [69]. Estahbanati et al. [59] reported that the maximum amount of hydrogen produced is around a pH of 4 in the presence of Pt/TiO₂ for the use of ethanol, methanol, and glycerol as sacrificial agents. The thermal activation energies in these systems are typically less than 30 kJ mol⁻¹, indicating milder activation steps compared to conventional catalytic reactions, such as product desorption and photoexcited carrier migration.

2.3. Electrolysis

Nowadays, water electrolysis represents the most developed sustainable and clean hydrogen production process, but it covers only 4% of industrial hydrogen production processes globally due to economic issues [70]. In fact, even when utilizing noble metal-based catalysts (Pt, Ru, Ir), the low kinetics of water oxidation, which implies high cell voltage (i.e., high energy consumption), makes this technique expensive and not competitive with the main hydrogen production method from natural gas [71]. Therefore, using bio-alcohols as hydrogen carriers in an electrolysis cell can be an interesting alternative, since their reversible oxidation potentials are much lower than that of water (ca. 0.1 V against 1.23 V under standard conditions), so the cell voltages or hydrogen production are lower (and so is the energy consumption) [72]. Methanol [73], ethanol [74], glycerol [75], and ethylene glycol [76] have been considered for hydrogen production through their electrolysis in proton exchange membrane electrolysis cells (PEMECs).

Figure 5 shows the principal of electrochemical decomposition of a bio-alcohol on a PEMEC. Taking ethanol as an example, it is fed to the anode and completely oxidized in the

presence of water, releasing CO₂ and protons (H⁺) (11). The protons that reach the cathode compartment, after crossing over the membrane, are reduced to H₂ (12).

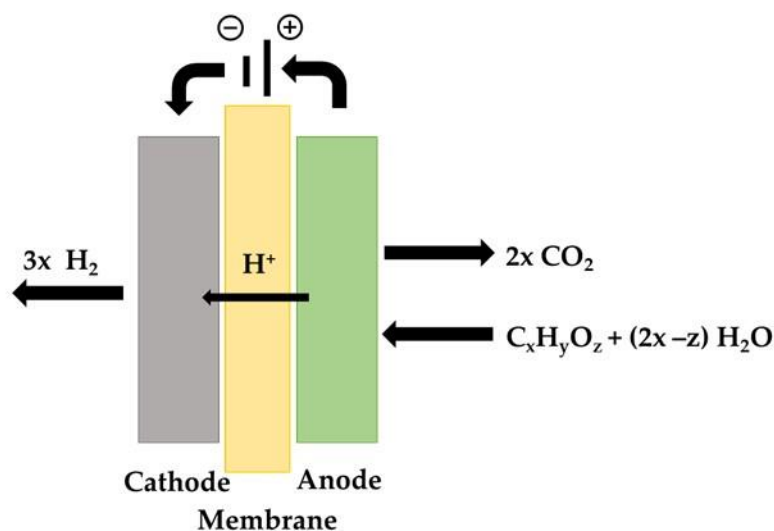
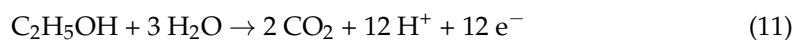
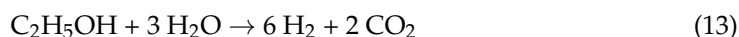


Figure 5. Schematic representation of the electrolysis process of bio-alcohols and oxygenated hydrocarbons.

This corresponds to the electrochemical reforming of ethanol into hydrogen and carbon dioxide, according to the overall reaction:



Both water and ethanol electrolysis require external energy; however, the energy needed for ethanol is less than that for water ($\Delta H = +58$ kJ/mole H₂ for ethanol vs. $\Delta H = +286$ kJ/mole H₂ for water) [72]. The lowering of cell voltage is required to boost the energy efficiency of an alcohol PEMEC. The decrease in cell voltage corresponds directly to the increase in the rate of electrochemical reactions happening at both electrodes, with a particular emphasis on the anode, where alcohol oxidation takes place [71]. Unfortunately, the electrooxidation of ethanol is a slow process with overpotentials of 0.3–0.4 V. Furthermore, platinum is known to be rapidly poisoned on its surface by adsorbed species (CO_{ads}) formed by alcohol dissociative adsorption [77]. To prevent this phenomenon, one approach is to modify the electrode by introducing oxygenated species (e.g., OH_{ads}) that are generated through the dissociation of water at lower potentials. This modification facilitates the complete oxidation of CO_{ads} species to carbon dioxide [78]. It has generally been found that combining Pt with other metals, such as Ni, Ru [74,79], Rh [71,72], Co [80], and Sn [81–84], in bi- and tri-metallic [85,86] catalysts increase the electrochemical performance of the anode, lowering the rate of catalyst deactivation. Nickel-containing Pt-based catalysts have demonstrated better electrochemical performance compared to other well-studied promoters such as Ru, especially at high potentials, while also being cost-effective [87]. A Pt-Ni-based anodic catalyst supported by graphene nanopatterns has been recently developed by Serrano-Jiménez et al. [88], achieving competitive current density and energy consumption.

As reported above, if ethanol is produced from renewable sources or organic waste, the process can contribute to a carbon-neutral balance. Moreover, bioethanol is relatively easy to obtain from renewable sources and thus has abundant availability. Table 2 shows the

advantages and disadvantages, costs, and efficiency of the different investigated methods for hydrogen production from bio-ethanol.

Table 2. Pros and cons, costs, and yield for hydrogen production by ethanol.

H ₂ Production Process from Ethanol	Advantages	Disadvantages	Performances	Ref.
Steam Reforming	<ul style="list-style-type: none"> ✓ Well-established and extensively used ✓ Large-scale applicability ✓ Higher selectivity compared to PO_x and ATR 	<ul style="list-style-type: none"> ✗ Coke formation and deactivation of catalyst ✗ High heat requirements 	H ₂ Yield: 60–95% EtOH Conversion: 90–100% H ₂ Selectivity: 70–90% @Ni/Al ₂ O ₃ , 250–500 °C, H ₂ O/EtOH = 3–6 H ₂ production cost: 1.58–2.6 USD/kgH ₂	[19,45,89,90]
Partial Oxidation	<ul style="list-style-type: none"> ✓ Temperature lower than SR and ATR ✓ Quick response time and fast start-up 	<ul style="list-style-type: none"> ✗ Lower ratio of H₂/CO ✗ Higher reaction temperature than ESR 	H ₂ Selectivity: 60–97% EtOH Conversion: @Noble metal/Al ₂ O ₃ , 500–600 °C, H ₂ O/O ₂ /EtOH = 3/0.3/1	[91,92]
Autothermal Reforming	<ul style="list-style-type: none"> ✓ Thermal neutrality ✓ High H₂ selectivity ✓ No external heat supply 	<ul style="list-style-type: none"> ✗ Complexity process ✗ High cost ✗ Higher reaction temperature than ESR 	H ₂ Yield: 47–94% EtOH Conversion: 84–97% @Rh/Al ₂ O ₃ H ₂ Selectivity: 40–60% @Pt/Al ₂ O ₃ 400–600 °C, H ₂ O/O ₂ /EtOH = 3/0.3/1	[93,94]
Photocatalysis	<ul style="list-style-type: none"> ✓ Renewable primary energy source ✓ High energy efficiency ✓ Applicability at a small scale 	<ul style="list-style-type: none"> ✗ Expensive catalysts ✗ Sensitivity to environmental condition ✗ Limited hydrogen production rate 	H ₂ production rate: 30–34 mmol/gh @Pt/TiO ₂	[95,96]
Electrocatalysis	<ul style="list-style-type: none"> ✓ Scale flexibility ✓ Co-generation of electricity and hydrogen 	<ul style="list-style-type: none"> ✗ Expensive catalysts ✗ Energy losses ✗ Need for continuous and constant electricity 	H ₂ volume: 102 mL @Pt/C, 20 °C j = 50 mA/cm ⁻²	[72]

The production of hydrogen from ethanol entails several distinct technologies, each with their own advantages and challenges. The decision on which method to utilize depends on factors such as scalability, economics, and efficiency. Therefore, it is essential to continue research and development in order to overcome limitations. Sustainable hydrogen production is of utmost importance. Progress in catalyst development, process optimization, and cost reduction may revolutionize ethanol-based hydrogen production, making it economically feasible and environmentally sustainable.

Several methods for hydrogen production, starting with light alcohols, have been investigated in this section. In this scenario, we propose a novel hydrogen production process, recently patented [97], so-called cyan hydrogen, from bio-alcohols and sodium metaborate, a by-product of little industrial interest, as a valid alternative. This name is inspired by a combination of the green and blue processes, due to the key role played by water and the low carbon content in the gas phase, respectively. The developed process

is constituted by a sequential discontinuous step in which bio-alcohols and water are alternatively fed to the sodium metaborate. Recently, we demonstrated the feasibility of the process in the presence of ethanol [98]. The process results in the simultaneous production of a hydrogen-rich stream (98% *v/v*) and a polymeric compound with a repetitive carbon pattern, $-\text{CH}_2-\text{CH}_2-$, i.e., polyethylene structure.

3. Hydrogen Storage

One of the primary issues hindering the advancement of hydrogen-based technology is storage. Thus, convenient, effective, and safe storage solutions must be sought to employ hydrogen as a zero-carbon fuel for worldwide decarbonization by 2050. It is crucial to first examine the properties of hydrogen to understand why the storage of hydrogen is a critical process throughout the H_2 production and management cycle. Among all chemical fuels, hydrogen has the largest gravimetric energy density. However, since current storage options require too much space, their low volumetric density prevents them from being used in transportation applications. One of the challenges is to increase volumetric density, which is achieved using a variety of conventional and innovative techniques [99–101].

3.1. Traditional and Innovative Methods for Hydrogen Storage

The state-of-the-art in hydrogen storage can be classified into physical-based and chemical-based methods (Figure 6). Physical techniques include compressing hydrogen at high pressures (200–700 bar), cryogenic storage (at $-252.8\text{ }^\circ\text{C}$), and cryo-compressed hydrogen. Compressed storage leads to a large hydrogen volume, making it less practical than methane or gasoline. Carbon-reinforced composite tanks improve safety but increase costs. Cryogenic liquid storage, a well-known and used technique, has lower volume requirements than methane but has energy-intensive liquefaction that uses around 35–40% of the gas energy. Moreover, hydrogen is stored at a temperature close to its phase transition point; hence, any rise in temperature leads to some of the hydrogen evaporating (known as boil-off). This evaporation reduces the system efficiency, consequently creating a significant hazard in unventilated environments [102]. A more recent technique involves storing compressed hydrogen at cryogenic temperatures, resulting in supercritical hydrogen known as cryo-compressed hydrogen. High-density storage of hydrogen is achieved, similar to liquid hydrogen but without the need for liquefaction, thereby eliminating evaporation losses [103]. Again, the high cost, although lower than that of compressed gas storage facilities, and the high energy consumption are among the disadvantages.

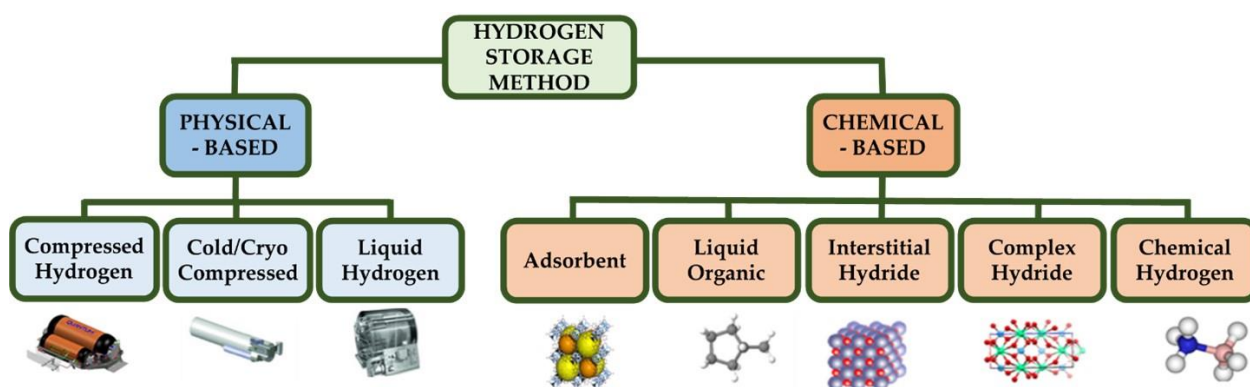


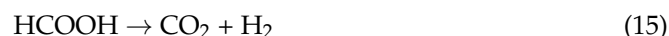
Figure 6. Physical and chemical-based technologies for hydrogen storage.

Therefore, innovative approaches are being explored to make hydrogen storage more adaptable and cost-effective for achieving Net Zero goals. These innovative options for hydrogen storage include hydrogen carriers that use physical or chemical bonding with another substance. Adsorption on high-surface-area materials is a promising technology, e.g., metal-organic frameworks (MOOFs) and microporous aluminosilicates (zeolites). MOOFs can adsorb more than 8–10 wt.% hydrogen at $-196\text{ }^\circ\text{C}$ but require additives to

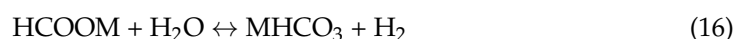
improve thermal conductivity. Metal-hydride technology, in which hydrogen is adsorbed and released by metal alloys, is another approach. This method is heavy and expensive due to the materials and lack of economies of scale. Scaling up production can increase costs due to material scarcity [100,104–106]. Similar to metal hydrides, chemical hydrides chemically bond hydrogen, but their properties differ from metal hydrides because they are made up of lighter elements. The most important difference is that most chemical hydrides are liquid under normal conditions, which makes them easier to transport and store; for this reason, they are known as liquid organic hydrogen carriers (LOHC). Due to chemical bonding, the hydrogen reacts and binds to another molecule (e.g., N-ethylcarbazole, dibenzyltoluene, formic acid, methanol, etc.), enabling storage at even atmospheric pressure and transportation of large amounts even at room temperature. The hydrogen is then released from the carrier by reversing the chemical process [107,108].

3.2. Liquid Organic Hydrogen Carriers (LOHC): Formic Acid and Formate

Formic acid (HCOOH, FA) is one of the most interesting chemical hydrides so far, despite having the lowest hydrogen storage capacity of 4.4% (by weight) gravimetrically and 53 kg/m³ volumetrically. This compound has some important advantages. The first is that dehydrogenation can be performed in a variety of mild conditions, even at room temperature [109]. The issue with formic acid is that it can also react by dehydrating and producing CO (14), which is poisonous to the catalyst, in addition to the dehydrogenation process, which produces CO₂ (15) consequently [110].



An alternative is represented using formates, the salts of formic acid; this technology is of interest, and the research group SaRAH, research is focused on the development of a catalyst that can work for the entire reactive cycle and therefore not deactivate in a short time. The reactive cycle foresees that the formates do not have dehydration as an adverse reaction; this will avoid the formation of CO. Also, when dehydrogenation occurs, no CO₂ is produced. These feature dehydrogenation (with reversible hydrogenation) as the only thermodynamically viable process (16).



where M = K⁺, Na⁺, NH₄⁺.

Metal formates release hydrogen and produce bicarbonates during dehydrogenation. With appropriate hydrogen pressure, the bicarbonates produced can be recharged into formates (Figure 7) [111].

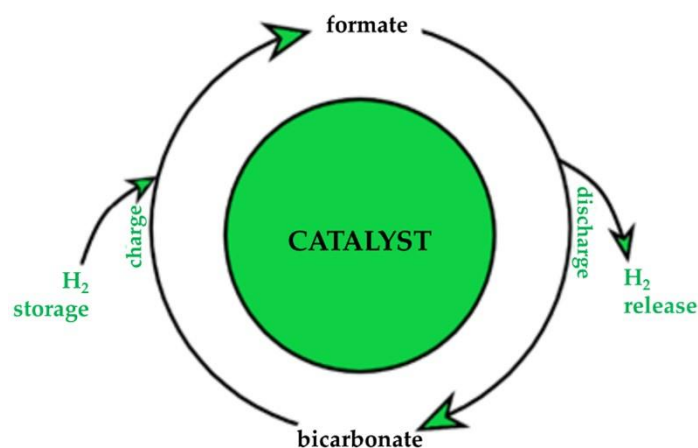


Figure 7. Cycle Formate/Bicarbonate for hydrogen storage in water solution.

Moreover, the formate-bicarbonate conversion has a free energy change of about zero ($\Delta G^\circ = 0$), meaning that even tiny changes in reaction temperature can effectively disrupt the equilibrium. Lastly, formates are non-corrosive and non-irritating, making them simple to handle even though they have a lower energy density than formic acid [112–115]. In Table 3, the comparison of volumetric density for formates storage with traditional storage in a cryogenic and compressed method is presented. The density is reduced by about 1/2–1/5. However, formate-based hydrogen storage is an option that can be pursued thanks to the obvious huge safety benefits. This review underlines the importance of (i) comparing the volumetric densities of the above-mentioned system with those traditions and (ii) identifying the most catalytic systems to exploit the potential of this technology [116].

Table 3. Volumetric density value for different hydrogen storage methods.

Storage Method	Volumetric Density (KgH ₂ /m ³)	Ref.
High-pressure (350 bar)	~20	[117]
Liquid H ₂	~20–50	[104]
Formate/Bicarbonate	~9.5	[116]

The conversion of formate to bicarbonate leads to the release of H₂, which is most favorable at elevated temperatures and reduced H₂ pressure. Nonetheless, in a closed vessel, the acceleration in H₂ partial pressure constrains the conversion of formate. However, in an open system, continuously releasing pure hydrogen at a constant pressure ensures theoretical unit conversions and enhances system efficiency. Although low temperatures and high pressure are thermodynamically favorable for bicarbonate hydrogenation, a relatively high temperature is required for catalyst activation and reasonable conversions to occur. Russo et al. [116] conducted thermodynamic modeling of the formate/bicarbonate interconversion and reported that a significant equilibrium conversion can be attained with H₂ at pressures ranging from 2 to 30 bar without reaching the critical levels. It is advantageous to perform the task at high salt concentrations, which are close to the solubility limits of hydrogen storage. Thermodynamics indicates that once the ideal operating conditions are found, the process may be operated to obtain high conversions. However, the lack of a catalytic system that can complete the transformation with kinetics suitable for the needed power currently restricts the deployment of the suggested technology in an operational way. The aim of this review is to present the state of the art to guide the development of catalysts that can optimize the dehydrogenation/hydrogenation cycle (15). The process must be cyclic to have potential from an industrial and application point of view. This means that the same catalyst must be used for both hydrogenation and dehydrogenation, which is why many authors have evaluated their catalysts for both reactions. Palladium is specifically mentioned as an active phase that can facilitate this reaction in transition metals. Palladium has demonstrated its performance potential in combination with other metals and with a range of substrates. Carbon substrates prepared and/or activated in various ways were of interest to the early research organizations [114,115].

Table 4 shows some of the catalysts studied in the literature with the respective yield values in both H₂ and formate and the values of the turnover number (TON) and the turnover frequency (TOF).

Table 4. H₂ and formate yields, TOF, and TON for different catalytic systems for hydrogen storage in formate/bicarbonate systems.

Catalyst	H ₂ Yield	TOF (h ⁻¹)	Formate Yield	TON	Ref.
Pd/C (from PANI)	-	2562	-	1625	[118]
Pd/C	-	5061	95.6%	1769	[119]
Pd/r-GO	96%	11,299	94.5%	7088	[120]
Pd/n, P-C	100%	3246	94.6%	4027	[121]
Ag/Pd/TiO _x /TiO ₂	-	6499	-	820	[122]

The synthesis of novel carbon-supported Pd nanoparticles made from polyaniline (PANI) was developed by Koh et al. [118]. They attained a turnover frequency (TOF) of 2562 h^{-1} for the dehydrogenation process at a temperature of $80 \text{ }^\circ\text{C}$ and a catalyst loading of 5000 ppm. The TON for the hydrogenation process, which was conducted under identical circumstances but with a $P(\text{H}_2) = 4.0 \text{ MPa}$, was 1625. Based on these preliminary results, Su et al. [119] modified the reaction duration and salt concentration and worked on the ammonium formate (HCOONH_4 , AF) with a Pd loading of 5 wt.% on activated carbon. A plateau was seen in the dehydrogenation process at $t = 1.5 \text{ h}$, yielding a TOF maximum of 5061 h^{-1} . $T = 20 \text{ }^\circ\text{C}$, $P(\text{H}_2) = 2.75 \text{ MPa}$, and varying the reaction duration from 1 h to 15 h resulted in a TON = 1769 and a formate yield of 95.6% for the hydrogenation process, respectively.

Bi et al. [120] developed a novel method utilizing Pd/r-GO with palladium as the catalyst's active phase. The study team experimented with several metal concentrations on the substrate for the dehydrogenation process; the optimum concentration was 1 wt.% Pd/r-GO, which produced hydrogen at a 96% yield and had a TOF of $11,299 \text{ h}^{-1}$. A TON = 7088 ($t = 10 \text{ min}$) and a formate yield of 94.5% were attained for the hydrogenation process operating at $T = 100 \text{ }^\circ\text{C}$, $P(\text{H}_2) = 4.0 \text{ MPa}$, 1 wt.% of Pd/r-GO, 6800 ppm catalyst, and a reaction time $t = 32 \text{ h}$. An increase in catalytic activity may be achieved by co-doping carbon materials with N and a second heteroatom, according to theoretical and experimental research by Shao et al. [121] Pd/N and P-C are more efficient than single-doped carbon materials. After 2 h of reaction time and a TOF of 3246 h^{-1} for the dehydrogenation process with a catalyst loading of 5000 ppm at 4.7 wt.% of Pd/N, P-C, at $T = 80 \text{ }^\circ\text{C}$, a unit H_2 yield could be produced. As a result, the reported yields of formate and TON for the hydrogenation process at $T = 80 \text{ }^\circ\text{C}$, with a $P(\text{H}_2) = 8.0 \text{ MPa}$ and a catalyst loading of 5000 ppm at 4.7 wt.% of Pd/N, P-C, were 94.6% and 4027 for 1.5 h of reaction, respectively. Titanium dioxide, a highly reactive semiconductor activated by UV irradiation and employed in heterogeneous photocatalysis, has been the subject of several investigations as a support for the Pd active phase obtained via photodeposition methods. When Pd is alloyed with other transition metals, impacts are also visible. Following this approach, S. Masuda et al. [122] created a catalyst based on a Pd/Ag alloy modified with a TiO_x shell supported on TiO_2 ($\text{Ag/Pd/TiO}_x/\text{TiO}_2$) to increase catalytic activity. Sodium formate (HCOONa , SF) is dehydrated with a TOF of 6499 h^{-1} at $75 \text{ }^\circ\text{C}$. Furthermore, the catalyst had strong activity and a TON of 820 during hydrogenation. The reaction was run at $80 \text{ }^\circ\text{C}$ with a loading of 1 wt.% Pd and 0.5 wt.% Ag.

Given that hydrogen must be delivered to a user at a pace appropriate for the needed power, hydrogen release kinetics are crucial for practical use. To provide quantitative indications of the maximum power that such a system may provide for different sizes and applications, Figure 8 shows the logarithm of the starting reaction rate against the logarithm of the storage vessel's volume along with iso-power curves for various applications [112].

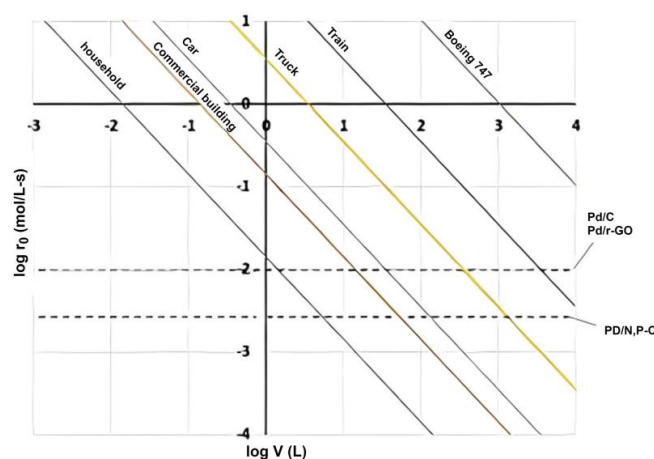


Figure 8. Initial reaction rate of reported catalysts against required storage volume for specific applications average power. Efficiency of the utilizer = 50% [112].

This comparison provides an overview of the potential performance of different catalytic systems in different practical applications. Some of the catalysts analyzed in the literature are already able to meet the energy demand for some applications, including household, commercial building, car, train, or truck power. These values must be considered as the starting point of a very promising technology that, therefore, still has a wide margin for improvement in terms of hydrogen release rate and solution storage density. This can allow the application of this technology in different applications in the sectors indicated but also on large-scale plants.

4. H₂ in Fuel Cells

Hydrogen fuel cells (HFCs) are electrochemical devices that directly transform the chemical energy of hydrogen and oxygen into power and heat. They are regarded as one of the most promising technologies for producing sustainable energy through hydrogen utilization, particularly for mobility and stationary uses [123].

The anode and cathode, the two electrodes that make up a fuel cell, are separated by an electrolyte that allows ion flow. Therefore, the device produces electricity by electrochemically oxidizing a fuel (such as hydrogen) at the anode and reducing an oxidant (such as oxygen) at the cathode. An external circuit is used to transport the electrons produced during the oxidation reaction to the cathode, creating an electric current (Figure 9) [124–126].

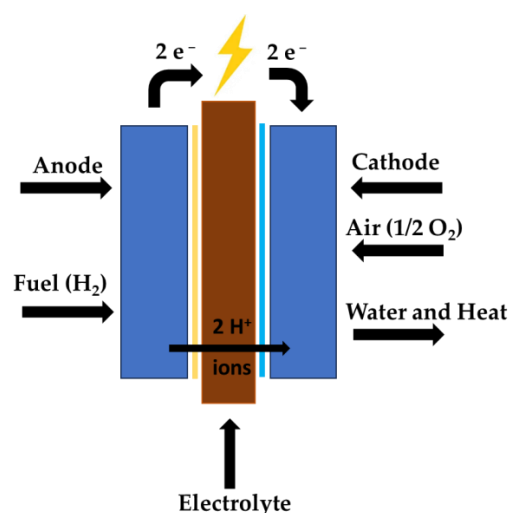


Figure 9. Operational principle of a fuel cell [127].

The electrolyte composition and operating temperature of fuel cells (FCs) are used for their classification (Table 5). Moreover, most of them can use H₂ as a fuel. Proton Exchange Membrane fuel cells (PEMFCs), Alkaline fuel cells (AFCs), and Phosphoric Acid fuel cells (PAFCs) are examples of hydrogen fuel cells, as shown in Table 5. On the other hand, Solid Oxide fuel cells (SOFCs) and Molten Carbonate fuel cells (MCFCs) can work with hydrogen and hydrocarbons. Table 5 covers FC classifications and their primary applications [127].

Table 5. Main applications of different types of hydrogen FCs.

Fuel Cells	H ₂ FC	Hydrocarbon FC	Bio-FC	LT-FC <200 °C	HT-FC >600 °C	Anode/ Cathode Catalysts	Electrolyte	Applications
PEMFCs	Yes	-	-	Yes	-	Platinum [128]	Polymer membrane	Transportation; Portable electronics; Backup power systems; Distributed power generation

Table 5. Cont.

Fuel Cells	H ₂ FC	Hydrocarbon FC	Bio-FC	LT-FC <200 °C	HT-FC >600 °C	Anode/Cathode Catalysts	Electrolyte	Applications
AFCs	Yes	-	-	Yes	-	Platinum, Silver, Nickel [129]	Alkaline electrolyte	Space missions; Industrial applications
PAFCs	Yes	-	-	Yes	-	Platinum [130]	Phosphoric acid	Combined heat and power plants
MCFCs	Yes	Yes	Yes		Yes	Nickel [131]	Molten carbonate	Large-scale power plants
SOFCs	Yes	Yes	-		Yes	Nickel [132]	Solid ceramic	Large-scale power generation; Military applications; Combined heat and power plants

fuel cell (FC), LT-FC (Low Temperature-fuel cell), HT-FC (High Temperature-fuel cell), Proton Exchange Membrane fuel cells (PEMFCs); Alkaline fuel cells (AFCs); Phosphoric Acid fuel cells (PAFCs); Molten Carbonate fuel cells (MCFCs); Solid Oxide fuel cells (SOFCs).

4.1. Comparison with Other Energy Conversion Systems Based on H₂

4.1.1. Internal Combustion Engines (ICEs) and Gas Turbines against Hydrogen Fuel Cells (FCs)

Compared to ICE, HFCs are more efficient, meaning that a higher proportion of the fuel they burn is converted into usable energy. However, fuel cells currently have a much higher initial cost than ICEs [133]. Gas turbines are more efficient than ICEs at converting chemical energy in fuel into mechanical or electrical energy. However, they are limited by their high NO_x emissions [124] and their inability to adapt to changing power demands. In addition, the Carnot theorem limits their efficiency because they use thermal energy to convert chemical energy into mechanical energy.

4.1.2. Hydrogen Fuel Cells vs. Batteries

Unlike batteries, HFCs offer significantly higher energy densities. This means that they can store and release a greater amount of energy per unit of weight or volume. In addition, HFCs tend to have a longer lifetime than batteries because they do not degrade over time. However, it's worth noting that fuel cells have a lower power density than batteries, which limits their ability to discharge energy quickly. In addition, fuel cells are much more difficult and expensive to produce due to their high complexity [134]. However, some researchers [124] also emphasize that the environmental benefits of fuel cells depend on the method of H₂ fuel production. Indeed, if H₂ is derived from fossil fuels, the overall environmental footprint of the fuel cell system may not represent a significant improvement over internal combustion engines (ICEs) or gas turbines (GTs). Conversely, if H₂ is produced from renewable resources such as solar or wind power, the fuel cell system may be an exceptional environmentally friendly option.

4.1.3. Solar and Wind Energy against Hydrogen Fuel Cells

In contrast to solar and wind energy, which rely on sunlight and wind availability, HFCs can generate a consistent power supply regardless of weather conditions. However, the production, storage, and transportation of hydrogen for FCs tend to result in higher environmental concerns associated with solar and wind power. Moreover, in terms of energy costs, solar and wind power are notably more affordable than fuel cells [135,136].

Overall, this comparison highlights that HFCs represent a promising technology for clean and efficient energy conversion, particularly when renewable or low-carbon hydrogen is utilized. Nevertheless, their lower energy density and higher cost in comparison to fossil

fuels remain challenges that need to be addressed, potentially limiting their applicability in certain scenarios.

4.2. Main Advantages and Disadvantages Related to FCs

The benefits of operating with FC include [124,137]:

- I. High efficiency. Since FCs directly convert chemical energy into electrical energy, they can reach higher efficiencies than energy conversion systems based on conventional combustion, up to 60%.
- II. Low emissions. FCs produce fewer emissions compared to traditional fossil fuel-based energy systems, making them a more environmentally friendly option. Indeed, hydrogen fuel cells (HFCs) emit only water vapor and heat as by-products; accordingly, they stand as a clean energy source. Furthermore, unwanted byproducts such as NO_x and SO_x or particulate emissions, are theoretically eliminated.
- III. Quiet operation: FCs operate quietly compared to traditional fossil fuel-based energy systems. This makes them an attractive option for applications where noise pollution is a concern, such as residential areas.
- IV. Modular design: FC systems can be designed and scaled to meet a variety of energy demands. This allows for the customization of fuel cell systems to meet the specific energy needs of different applications.

On the other side, the disadvantages of using FC include [124,137]:

- V. High costs: FC systems can be costly to develop and deploy, limiting their widespread use. The cost of fuel cell systems is caused by several factors, including material costs, manufacturing methods, and a lack of economies of scale.
- VI. Limited durability: Due to their limited durability, fuel cells may require frequent maintenance and replacement, thus increasing their lifecycle cost. This is due to their sensitivity to temperature, humidity, and pollutants, all of which can have an impact on their function over time.
- VII. Hydrogen storage and distribution safety issues: Hydrogen storage and distribution is a critical obstacle for the development of fuel cell technology. Hydrogen is a highly combustible gas that must be handled and stored with caution.
- VIII. Inadequate infrastructure: The absence of infrastructure to support fuel cell technology, such as hydrogen refueling stations, as well as the high costs associated with their setup and maintenance, hinder widespread implementation.

4.3. Challenges (Pt Replacing, Design Parameters, and Scalability)

Two main challenges must be addressed to enable the widespread diffusion of FC technology: cost reduction and stability improvement. The main factors affecting costs involve the use of rare and expensive raw materials as well as complex manufacturing processes that require specialized equipment.

At the same time, great efforts have been made towards the development of more active electrocatalysts, which are bound to play a key role in determining cell efficiency and operating time.

Pt-based electrocatalysts are currently the most effective materials for the oxygen reduction reaction (ORR), yet their high cost, poor stability, and limited availability make them unsuitable for large-scale commercial applications [138]. In addition, the presence of some species, such as sulphur compounds or carbonaceous species such as carbon monoxide (CO), in Pt-low-temperature fuel cells could cause the poisoning of the site. Indeed, these species permanently absorb onto platinum and cover reaction sites, thus limiting the desired electrochemical reactions [139].

As a result, there has been significant interest in the development of non-Pt-based electrocatalysts for the ORR. Notably, nitrogen-doped carbon nanotubes have disclosed a higher ORR activity than Pt-based electrocatalysts in alkaline solutions [140]. Even iron-doped carbon materials can exhibit a higher ORR performance than Pt-based electrocatalysts in acidic solutions [141].

However, there are still several challenges associated with the use of non-Pt-based electrocatalysts. For example, these materials can be susceptible to degradation over time, which can limit their durability and performance.

In addition, the synthesis of these materials can be complex and requires careful optimization to ensure that the resulting material has the desired properties.

To address these issues, a huge chance comes from the bioinspired approach, which draws inspiration from nature and usually uses bioavailable materials. Nature-inspired materials exhibit unique features, including extended porous architectures, high surface areas, considerable mechanical and thermal stabilities, large abundance, and cost-effectiveness. These beneficial properties make them potential candidates for the design and fabrication of different components of FCs, including electrolytic membranes as well as highly efficient heterogeneous catalytic electrodes, able to overcome the challenges of well-known Pt/carbon catalysts [142].

Among nature-inspired materials, biomass has emerged as a cheap source of carbon-based materials. In the limited-oxygen condition, biomass can be thermochemically converted to biochar, which presents around 54–93% of carbon but also nitrogen and phosphorus heteroatoms, which are able to enhance the electrochemical properties [143]. Indeed, P and N groups have been demonstrated to be effective inhibitors of carbon electro-oxidation, improving electrocatalyst performance.

Indeed, carbon-based materials can contain metallic impurities even without the direct involvement of metals during their synthesis process. However, these impurities can significantly improve or impair the electrochemical performance of carbon-based materials [144]. On the other hand, the excessive use of biomass can damage the environment and ecosystem, raising ethical concerns related to the use of large amounts of ground for non-edible cultivation. A common disadvantage of biomass is its high moisture content, which can cause some problems in biomass conversion, such as poor combustion and sedimentation of various compounds during biomass drying. In addition, the presence of high contents of alkaline and halogen elements in biomass can cause environmental problems, such as the release of dangerous compounds [145]. A further major issue in biomass conversion is the existence of toxic trace elements such as Ag, Be, Cd, and Hg, which can increase volatilization and limit retention and capture performance during biomass pyrolysis [146]. In summary, biomass costs increase due to collection, transport, and storage costs, while its reliability is uncertain due to factors such as fluctuating crop production, natural disasters, and seasonal variations, leading to potential changes in biomass quality.

4.4. Biowaste as the Most Sustainable Choice for Carbon Electrocatalyst Production

Waste materials are an abundant and cheap source of biomass, which holds promise as raw materials for producing electrocatalysts and electrolytes in FCs, as shown in Table 6 [145,147,148].

By recycling and utilizing bio-waste, which is an abundant, inexpensive, safe, and environmentally friendly source of carbon, FC production can be made more cost-effective and environmentally sustainable. Biowastes can be used as templates to produce porous electrodes or can be thermally degraded to produce carbonaceous materials with high surface area, porosity, and good electrical conductivity, making them suitable as supports for metal or metal oxide nanoparticles or as non-precious metal catalysts.

Examples of biowastes include agricultural/animal residues or municipal/forest waste, as shown in Table 6 and in Figure 10 [149,150].

For instance, eggshell membrane (ESM) templates have been used to fabricate highly crystalline perovskite ceramics for SOFCs, resulting in increased power density [151]. Three-dimensional (3D) interwoven fibrous cathodes made from $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSC)/ $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC) SSC/SDC exhibited higher maximum power densities in SOFCs due to lower electrode polarization resistances and cell ohmic resistances [152].

Several studies [153] reported that waste tires or coconut shells can be processed to produce activated carbon, which is then used as an electrode material in a microbial fuel cell.

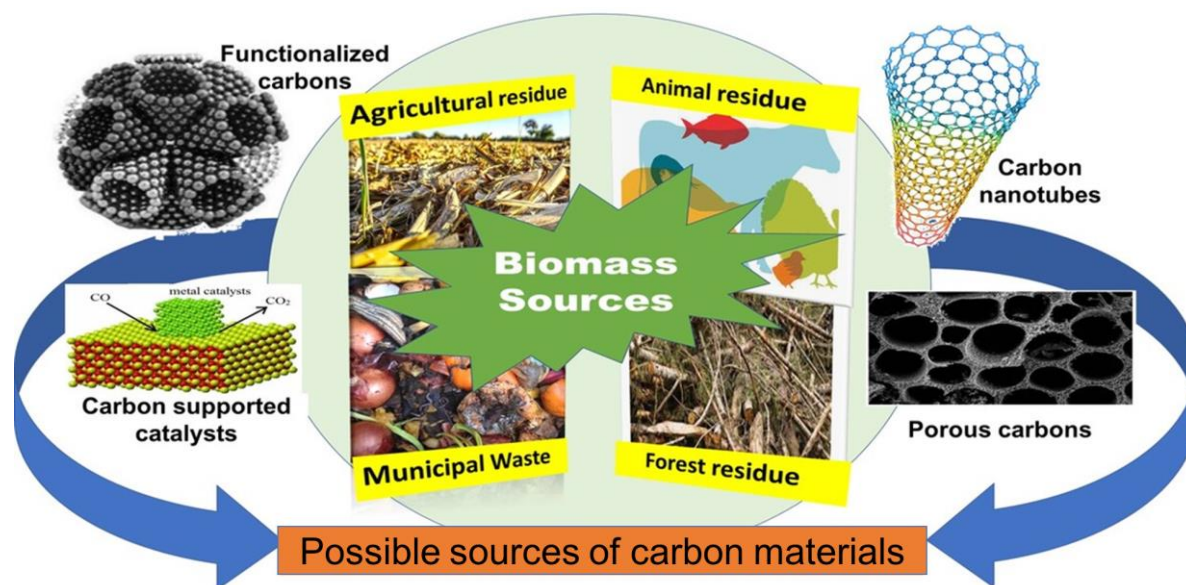


Figure 10. Schematic representation of the most possible sources of biomass [150].

Nitrogen and sulfur co-doped bio-carbon floes (NSC) have been obtained by thermally decomposing a zinc-based metal-organic coordination polymer (MOCP-Zn) synthesized from chicken feather-derived polypeptides [154,155]. The synthesis of polypeptides involved washing the chicken feathers with acetone, followed by treatment with aqueous ammonia to degrade them into polypeptides. The resulting ammonia solution containing polypeptides was dried and milled into powder. The NSC catalyst showed great potential for application in PEMFCs due to its high electrocatalytic activity for oxygen reduction reaction (ORR) in both alkaline and acidic conditions. Linear sweep voltammetry (LSV) results indicated that NSC-3.5 (3.5 indicates the pH value of powder precursor synthesis) had a larger diffusion-limited current density than Pt/C and a high ORR kinetic current density ranging from 5.89 to 8.11 mA cm⁻² at a potential range of 0.3–0 V. Moreover, NSC-3.5 demonstrated superior stability in an acidic medium compared to Pt/C. In another study, orange peel was chemically activated with H₃PO₄ to prepare activated carbon (AC), onto which Pt was deposited [156]. The resulting Pt/OP-AC electrocatalyst exhibited acceptable performance as a catalyst support for ORR in PEMFCs, with an electroactive surface area of 17.8 m² g⁻¹. The Pt/OP-AC cathode electrode in fuel cell tests achieved a power density of 19 mW cm⁻² with O₂ and H₂ flow rates of 1000 mL min⁻¹ at 60 °C [154,155].

Lignin-derived activated char could also be used to produce metal-nitrogen-carbon (M-N-C) electrocatalysts as a reliable substitution for platinum-group metals (PGMs) for the ORR in the fuel cells [157]. Moreover, the development of M-N-C catalysts can be further economized by consuming waste biomass as an inexpensive carbon source for the electrocatalyst support.

Zhao et al. showed that the waste lignin can be valorized through pyrolysis to obtain char with a very high surface area. The obtained biochar was then functionalized with Fe-, Mn-, and Fe-Mn phthalocyanine to produce monometallic and bimetallic M-N-C electrocatalysts with good ORR performance [158].

The integration of the FeMn-catalyst in a PEMFC reached a maximum power density of ~72 mW cm⁻², while its AEMFCs reached a maximum power density of ~261 mW cm⁻². Both PEMFCs and AEMFCs realized the translation of energy through the hydrogen oxidation reaction (HOR) at the anode and ORR at the cathode. However, ORR is several orders of magnitude slower than HOR and imposes a much higher overpotential, restricting overall device efficiency. To deal with this challenge, PGMs are typically employed as electrocatalysts, but their use makes the application of fuel cells economically impracticable.

To make the most of the catalytic activity of PGMs, it is possible to aim for a higher catalyst surface area, thus using lower PGM loads. Indeed, a high surface area allows the

active sites to be better exposed, enabling good catalytic performance while using low metal loadings.

Among the possible technologies used, the electrospinning process represents a versatile approach for producing carbon electrodes from a precursor solution. Specifically, it is an electrodynamic process that allows for the obtaining of fibers characterized by a high specific surface area and an open pore structure. By using this approach, a renewable source of carbon has been proposed as a carbon-fiber precursor as well.

Electrocatalysts based on waste materials and prepared by electrospinning technology have shown promising results for H₂ fuel cells in terms of activity and stability. For example, nanofibers derived from coffee grounds have been reported to exhibit comparable or superior performance to commercial Pt/C catalysts for oxygen reduction reaction (ORR) at the cathode [159]. Furthermore, Lu et al. [160] showed that nanofibers derived from eggshells showed high activity and stability for the hydrogen evolution reaction (HER) at the anode. Moreover, nanofibers derived from orange peels are bound to show excellent performance for both ORR and HER in alkaline media [161].

Some authors [162] prepared lignin fibers with and without phosphorus and loaded with platinum (Pt) in a single step by means of electrospinning lignin/ethanol/phosphoric acid/platinum acetylacetonate precursor solutions, as shown in Figure 11 [163–165]. The electrospun fibers containing Pt particles showed outstanding catalyst performance in the electro-oxidation of methanol and ethanol. However, there are several challenges to overcome for the widespread use of electrospinning in producing electrocatalysts from waste materials for hydrogen fuel cells. These challenges include optimizing electrospinning parameters, scalability, long-term stability assessment, standardized characterization methods, and considering environmental and economic impacts.

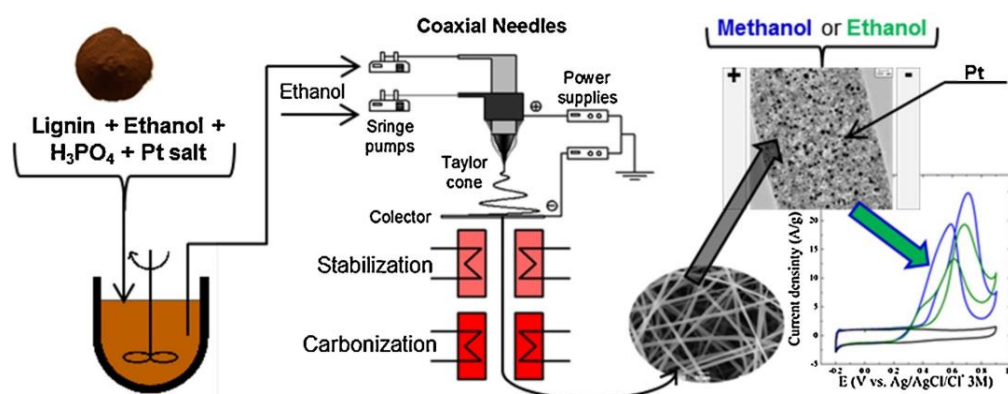


Figure 11. Lignin-derived Pt-supported carbon (submicron) fiber electrocatalysts for alcohol electro-oxidation [162].

Overall, the use of natural materials may have challenges which necessitates further studies [145].

The benefits of using waste materials as electrocatalysts are:

- I. Reduce the dependence on platinum and other precious metals;
- II. Improve the performance and durability of the electrodes by providing a larger surface area, good electrical conductivity, and high resistance to corrosion;
- III. Enhance the catalytic activity and selectivity by introducing heteroatoms (such as nitrogen, sulphur, or phosphorus) or functional groups into the carbon structure;
- IV. Lower the cost and environmental impact of fuel cell production by recycling and valorizing waste materials.

The negative aspects of using waste materials as electrocatalysts are:

- I. Low purity and uniformity compared to synthetic materials;
- II. Require additional treatments to remove impurities or contaminants that may affect the catalytic performance or poison the catalysts;

III. Limited availability or variability depending on the source and season.

Table 6. Biowaste as sources of raw materials to produce electrocatalysts or electrolytes in FCs.

Biowaste	Active Phase	Application	Performance	Ref
Peanut shell	Nitrogen-doped porous carbon	High-performance supercapacitors	-Specific capacitance: 310.59 F/g at 0.5 A/g (three-electrode system) -Specific capacitance: 300.6 F/g at 0.5 A/g (two-electrode system) -Specific capacitance: 246.4 F/g at 10 A/g (two-electrode system) -Capacitance retention: 81.98% from 0.5 to 10 A/g (two-electrode system) -Energy density: 40.92 Wh/kg at 990 W/kg (two-electrode system) -Cycle stability: 90.14% capacitance retention after 5000 cycles (two-electrode system)	[166]
Collagen	Nitrogen-rich carbon nano-onion architectures	Metal-free oxygen reduction reaction (ORR) catalyst	-Onset potential: ~0.32 V vs. Ag/AgCl in O ₂ ; -Saturated KOH solution; -4-electron transfer pathway for ORR; -Electron transfer number (n): ~4.1; -Comparable performance to the Pt/C catalyst; -Immunity to methanol crossover poisoning; -Excellent operation stability; -Durability and stability confirmed;	[167]
Pomelo peel	Nitrogen-doped porous carbon	ORR applied to fuel cells and metal-air batteries	Half-wave potential (0.86 V vs. RHE) and the kinetic current (10.40 mA/cm ²), which are much higher than those obtained from the Pt/C (0.83 V, 5.22 mA/cm ² , respectively)	[168]
Euonymus japonicus leaves	Nitrogen self-doped porous carbon nanosheets (NPCNS)	ORR and OER Electro-catalytic applications such as fuel cells or metal-air batteries	-ORR activity: onset potential of NPCNS-900 is 0.98 V vs. RHE (more positive than commercial Pt/C catalyst, which is 0.95 V); -OER performance: overpotential of NPCNS-900 is only 1.57 V vs. RHE (current density of 5 mA/cm ² , lower than commercial Pt/C, >1.7 V); -Enhanced methanol tolerance compared to commercial Pt/C for ORR	[169]
Tea residue	N and F co-doped porous carbon materials	ORR	-Heteroatom (N and F) doping facilitates charge redistribution and electron transfer in ORR; -Higher limited current density and electron transfer number (about 3.8) compared to Pt/C	[170]
Poultry bio-waste	Activated carbon electrocatalyst (different chemical activators (KOH, H ₃ PO ₄ , ZnCl ₂) combined with heat treatment)	ORR	Onset potential changing from -0.02 to -0.20 V; ORR current density (J _{ORR}) at 0.4 V (mA cm ⁻²) changing from 0.3 to 1.7	[171]
Biogas	Solid Oxide fuel cell (SOFC)	Electricity generation	SOFC performance improvement with increasing reforming temperature; Ability to achieve 100% renewable operation in a hybrid power plant	[172]
Egg	Heteroatom-doped mesoporous carbon	Oxygen reduction in microbial fuel cells	ORR potential: +0.10 V, onset potential: +0.257 V (vs. Ag/AgCl); Electron transfer number: 3.84–3.92 (indicating a four-electron pathway); Maximum power density: 737.1 mW m ⁻² (comparable to MFC-Pt/C at 704 mW m ⁻²)	[173]
Cattle bones	Nitrogen and phosphorus co-doped hierarchically porous carbon (N,P-HPC)	ORR	ORR onset potential: 0.924 V (comparable to commercial Pt/C) ORR half-wave potential: 0.853 V (12 mV higher than that of Pt/C) ORR kinetic current density: 38.2 mA cm ⁻² at 0.8 V (1.9 times that of Pt/C); Superior electrochemical stability and methanol tolerance compared to Pt/C.	[174]
Tea residue	Nitrogen and fluorine co-doped carbon (T-NFC)	ORR	ORR-limited current density is higher than commercial Pt/C; ORR electron transfer number of about 3.8 (indicating an efficient ORR mechanism); Enhanced methanol tolerance in alkaline medium compared to Pt/C; Catalyst with high catalytic activity, excellent stability, and high selectivity	[170]

Table 6. Cont.

Biowaste	Active Phase	Application	Performance	Ref
Soybean straw	Honeycomb-like Fe-N co-doped porous carbon (Fe-N-PC)	Fuel cells	ORR performance alkaline: Onset potential: 0.989 V; Half-wave potential: 0.854 V; (Comparable to commercial Pt/C catalyst) ORR performance is acidic: Onset potential: 0.886 V; Half-wave potential: 0.754 V; (Superior to many other Fe and N-doped electrocatalysts)	[175]
Golden Shower Pods biomass (GSP)	N-doped porous carbon (N-PC)	Oxygen Reduction Reaction (ORR); Oxygen Evolution Reaction (OER); Hydrogen Evolution Reaction (HER)	ORR: four-electron pathway (average $n = 3.6$), Tafel slope of 86 mV dec^{-1} , half-wave potential of 0.76 V ; OER: better overpotential values (314 mV at 10 mA cm^{-2}), Tafel slope of 132 mV dec^{-1} ; HER: better overpotential values (179 mV at 10 mA cm^{-2}), Tafel slope of 98 mV dec^{-1}	[176]
Shrimp-shell	N-doped porous carbon (NPC-800); N-doped carbon nanodots (N-CNs); N-CNs@SiO ₂ composite subjected to thermal evaporation	ORR	ORR: onset potential of 0.06 V , Half-wave potential of 0.21 V , limiting current density of 5.3 mA/cm^2 (at $0.4 \text{ V vs. Ag/AgCl}$) Comparable to commercial Pt/C catalyst: onset potential of 0.03 V ; half-wave potential of 0.17 V ; limiting current density of 5.5 mA/cm^2 (at 0.4 V); Superior durability and high methanol tolerance in alkaline media, better than commercial Pt/C catalyst	[177]
Seaweed	Fe ₂ N/C ORR catalyst	ORR in alkaline fuel cells	Outperforms Pt in ORR activity, stability, and methanol tolerance in alkaline media. Onset potential of 0.82 V vs. RHE in 1 M HClO_4 solution is comparable to Pt/C (0.91 V vs. RHE). Superior electrical conductivity.	[178]

In this field, the SaRAH group is exploring green strategies based on electrospinning with the aim of obtaining carbon fibers with a fine distribution of platinum active phase, which should be used as electrocatalysts with enhanced stability and activity for fuel cell applications. Notably, bioderived polymeric materials have been used for the preparation of electrodes for fuel cell applications. No additional material was added to the system except the platinum salt used as a precursor.

5. Conclusions

This review addresses the urgent need for a transition to sustainable and clean energy solutions by providing an in-depth analysis of state-of-the-art technologies and the major challenges to be faced in the main pillars of the H₂ cycle.

The first part of this review is focused on H₂ production and highlights the potential of using bio-alcohols from renewable sources for carbon-neutral processes. By exploring various methods, including ethanol steam reforming, partial oxidation, autothermal reforming, photocatalysis, and electrocatalysis, this approach offers a promising route to cleaner energy production. Hydrogen production from alcohols presents an attractive opportunity, yet the industry confronts significant obstacles before it can establish itself as competitive and environmentally viable on a large scale. Crucial to scaling up to meet the growing demand for hydrogen, particularly in transitioning towards a hydrogen-based economy, is refining reactor design and optimizing the development of new catalysts. Continual research and development are vital to surmounting these obstacles and actualizing the complete capacity of hydrogen as an energy transporter.

The second part looks at innovative methods of hydrogen storage, with a particular focus on formic acid as a sustainable alternative. Formate, derived from CO₂ or lignocellulosic biomass, provides a renewable route to high-purity hydrogen synthesis. This sustainable approach could significantly reduce the carbon emissions associated with conventional

storage methods. As explained in this paper, the hydrogen storage technique through the reactive cycle formates/bicarbonates is one of the challenges of the future, being highly safe, economical, and usable in different applications. In order for the proposed technology to be marketed and used on a large scale, it will be necessary to increase the storage density of the system—increasing the concentrations of reagent salts and evaluating the possibility of working in a heterogeneous system—and increase the kinetics of both reactions.

The third and final part examines the use of hydrogen in fuel cell technologies. The versatility of hydrogen in replacing traditional fossil fuels in various sectors, including transport, heat, industry, and electricity, is emphasized. Nature-inspired materials, such as bio-waste, offer an interesting avenue for creating efficient porous electrodes in fuel cell applications. Technologies such as electrospinning and spincoating hold promise for converting biowaste into high-performance photoelectrocatalysts, further advancing the use of hydrogen in clean energy production. Future developments will focus on an in-depth investigation of the electrocatalytic properties of the fibers to study the performance of the fibers as electrodes and will push towards the production of materials with a higher content of biowaste molecules to improve the circularity index, sustainability, and final functional properties.

Overall, this comprehensive review highlights the potential of hydrogen as a clean and versatile energy carrier while also highlighting the importance of sustainable approaches in every aspect of the hydrogen cycle. To achieve the ambitious targets, it is imperative that we continue to develop and optimize technologies for hydrogen production, storage, and utilization. By doing so, we can contribute to a more sustainable and environmentally responsible energy future for all.

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