Hydrogen Environmental Benefits Depend on the Way of Production: An Overview of the Main Processes Production and Challenges by 2050

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Hydrogen (H₂) is presented as an important alternative for clean energy and raw material in the modern world. However, the environmental benefits are linked to its process of production. Herein, the chemical aspects, advantages/disadvantages, and challenges of the main processes of H₂ production from petroleum to water are described. The fossil fuel (FF)-based methods and the state-of-art strategies are outlined to produce hydrogen from water (electrolysis), wastewater, and seawater. In addition, a discussion based on a color code to classify the cleanliness of hydrogen production is introduced. By the end, a summary of the hydrogen value chain addresses topics related to the financial aspects and perspective for 2050: green hydrogen and zero-emission carbon.

1. Introduction

Hydrogen is the smallest and lightest element in the periodic table (atomic ratio 13 pm and atomic mass 1.008), and surprisingly, it is the most abundant element in the whole universe. It is the tenth most abundant element on Earth (0.14%),[1] and it can be found in our atmosphere (0.6 ppm).[2] in water, in organic molecules, or other chemical compounds. In the same way, hydrogen can be found in large quantities in the sun.[3,4] Moreover, hydrogen represents 73.4% of the sun’s mass, being responsible for 85% of its energy, that comes from hydrogen atoms fusion, forming helium and releasing a huge amount of energy, ≈10[^4] J Year⁻¹.[5]

The first report of molecular hydrogen is dated at the beginning of the 16th century when a gas was identified as a product of the reaction between sulfuric acid and iron. This gas was first identified as a unique substance by Henry Cavendish in 1776; however, it was only named in 1788 by Antoine Lavoisier, who named the substance from the Greek roots “hydro” (water) and “genes” (creator). Since then, H₂ has been extensively studied and used for a wide range of applications.[6]

Nowadays, one of the most important applications of hydrogen is in the petrochemical industry, including hydrocracking (hydrogenation to produce refined fuels with smaller molecules and higher H/C ratios) and hydroprocessing (hydrogenation of sulfur and nitrogen compounds to further remove them as H₂S and NH₃) for the purification of petroleum and fuels. In addition, hydrogen is essential in the base industry especially through the synthesis of ammonia from the direct reaction with N₂ at high temperatures and pressure in the well-known Haber–Bosch process.[7] It is worth mentioning that ammonia is fundamental for fertilizers production and by the improvement of agricultural performance. Hydrogenation can also be applied to decrease the degree of unsaturation in fats and oils and on some fine chemical synthesis. Hydrogen has been used in the electronics industry as a protective and carrier gas, in deposition processes, for cleaning, in etching and reduction processes. Another example is its use in the metallurgical industry in the reduction stages and also in the direct reduction of iron ore, which involves the separation of oxygen from the iron ore using hydrogen and synthesis gas (syngas). A strategic application of the H₂ is to consider it as a fuel, being able to be applicable for direct combustion, by itself or in some blends with natural gas, and also in fuel cells (FCs), where it can provide a reliable and efficient energy power, that can be used in stationary power stations and also as a good candidate for transportation vehicles.[3,6,8–11] Although presenting great potential for several applications, according to a sense from 2018,[12] 51.70% of total H₂ worldwide is used for refining, 42.62% is used for ammonia production, and only 5.68% is used for other applications, including its use as a clean and renewable fuel.

Nevertheless, H₂ application as a renewable fuel is the most promising application for the future, and its main advantage is related to its cleanliness and low greenhouse gas emissions,
which is determined by the hydrogen production pathway (HPP). Therefore, the study and understanding of every HPP are essential for the development and advance of the so-called “hydrogen economy,” mainly focused on the use of green hydrogen. During the analysis of HPP, a few primary challenges must be conquered, such as the choice of the feedstock—(FF or water), the energy source needed to extract hydrogen from the feedstock, and the catalyst that is needed to overcome some kinetic and thermodynamic limitations that are present regardless of the process.[4,12,13] A meticulous study on how to overcome these challenges can help the development of an efficient and economically viable green HPP, which can contribute to a more sustainable future.

Due to these advantages and the extreme importance of hydrogen for our society, this review has presented a discussion about hydrogen production processes. First, H\textsubscript{2} was classified according to its color codes, which reflects how sustainable are the processes. After this, the reforming processes used for hydrogen production were described, highlighting the advantages and drawbacks. The same approach was used to describe the hydrogen produced from the water (electrolysis) where the technologies are converging to net-zero carbon emission goals, such as the green hydrogen. In addition, it included a detailed discussion about the source of water (wastewater and seawater) to hydrogen production, including biohydrogen. Technologies of hydrogen production outside the Earth were also included to motivate the scientific community to adopt new technologies. By the end, a summary of the hydrogen value chain addresses topics related to the financial aspects and perspective for 2050: green hydrogen and zero-emission carbon.

2. The Cleanliness Level of Hydrogen: Representation by Colors Code

The level of cleanliness of the energy produced from hydrogen is related to the amount of greenhouse gases produced during H\textsubscript{2} production. Furthermore, the sustainability of all energy chain also depends on the energetic input, the type of raw material, the design of the industrial process, and CO\textsubscript{2} emissions.[14,15] An interesting approach for classifying carbon emission during hydrogen production is the use of color labels. The color codes of the hydrogen production process might be the statement of sustainability from the suppliers to the consumers. This strategy allows a fast indication of the kind of hydrogen (in terms of carbon emission) you or a company are handling. Therefore, it is expected an environmental responsibility and greater competitiveness from H\textsubscript{2} suppliers by sustainable products.[16,17]

The first proposed model for the H\textsubscript{2} classification is based on three colors, according to the CO\textsubscript{2} emission, as shown in Figure 1. Gray H\textsubscript{2} is produced through the steam reforming process and uses FFs as a raw material. In addition, there is no restriction to carbon emission, and it is considered “dirty” hydrogen. The process to produce blue H\textsubscript{2} is similar to the gray one; however, the produced carbon is captured and stored, decreasing the CO\textsubscript{2} emissions. On the other hand, green hydrogen is considered as a renewable hydrogen due to the use of water as a source of H\textsubscript{2} and renewable energy (RE) in the electrolytic process (water splitting (WS) process), which fits with the zero-emission carbon approach. Figure 1 presents a comparative scheme of these three processes.[14,16,17]

The H\textsubscript{2} chain is plural and complex, and because of this, new color codes were added to improve the description of the cleanliness level of the hydrogen production. Based on this concept, a complete color codes table can be found in Figure 2.

The brown hydrogen (black hydrogen can be a synonym) is produced from coal in the gasification process, which generates large amounts of CO\textsubscript{2} and high environmental impact, even though the low cost of produced H\textsubscript{2} is hard to achieve. Gray and blue hydrogen were described before. Like the brown, blue, and gray hydrogen, turquoise hydrogen is also produced from FFs, but the methane pyrolysis at high temperature allows the carbon elimination in solid form, which reduces the CO\textsubscript{2} emission. The key point of this strategy is the source of energy used and its carbon emissions. In other words, if the input energy is renewable, the process would be clean. Thus, it can have a lower environmental impact (Figure 2).

![Figure 1. Scheme of three colors to classify the hydrogen production according to the carbon emission.](image-url)
Pink, yellow, and green hydrogen are produced from the electrolysis process (also known as water splitting (WS)), and they use water as a raw material. However, the final environmental impact also depends on the input energy. Pink hydrogen is obtained from the electrolysis process powered by nuclear energy, and yellow uses the same strategy, but the H\(_2\) is produced using the input of mixed origin (FF and renewable). Green hydrogen is produced by the cleanest process, where the water electrolysis is driven exclusively by RE.

The challenge for incorporation of the green hydrogen in the hydrogen chain is the cost. The price of sustainable hydrogen is approximately four times higher than those produced from the FFs process.

White color, for example, is used only to classify the H\(_2\) from natural origin, and due to the rare occurrence on the Earth, there is no commercial interest. This was the first proposal for the white H\(_2\). However, some authors have considered white hydrogen as a product of thermochemical WS produced by concentrated solar energy. In addition, the company Recupera has defined white hydrogen as H\(_2\) produced from plastic, biomass, or garbage. The definition of white hydrogen is still open.

As hydrogen color code is directly related to its production pathway, in the next section, we present a brief discussion on the main HPP, obtaining gray and blue hydrogen from FFs. And then, a discussion on the best ways of obtaining green hydrogen is presented, along with the main perspectives for the future applications of hydrogen production.

### 3. Fuel Reforming Processes

#### 3.1. Steam Methane Reforming

Steam methane reforming (SMR) represents the most important industrial pathway for large-scale production of H\(_2\), being responsible for \(\approx\)48% of the overall production of molecular hydrogen in the world. The technique itself consists of three fundamental steps: syngas generation (Equation (1)), water–gas shift (WGS) reaction (Equation (2)), and hydrogen purification. WGS is used to increase the hydrogen content and to convert CO into CO\(_2\), whereas in the final purification step, H\(_2\) and CO\(_2\) are separated by different methods. The following reactions occur when CH\(_4\) is used as feedstock:

\[
\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2; \quad \Delta H^{\circ}_{298K} = 206.4 \text{ kJ/mol (1)}
\]

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2; \quad \Delta H^{\circ}_{298K} = -41.2 \text{ kJ/mol (2)}
\]

As it is shown, the SMR is very endothermic. Thus, it is necessarily an external heat source, and usually, FFs are used to reach operating temperatures between 800 and 900 °C, which makes SMR a non-sustainable process. Also, the steam-to-carbon (S/C) ratio plays an important role in the efficiency of methane conversion, and after several attempts, an optimum value in which coke formation is prevented at high temperatures.

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**Figure 2.** Color codes of hydrogen. Complete comparison among the processes according to the CO\(_2\) emission, environmental impact, and cleanliness of the hydrogen produced; FFs = fossil fuels and RE = renewable energy.
(around 800 °C) was found to be in the range of 2.5–3.0, the steam being in excess.[27,29,30]

Even though high temperatures and elevated steam pressures reforming operation conditions are needed, a catalyst is still required to speed up the reaction due to the high stability of methane.[31–34] In this sense, Ni-based catalyst can lower the activation barrier, thus increasing the reaction rate.[32,33] However, these Ni-based catalysts may be poisoned by sulfur and by the deposition of carbon. The latter can block pore structure and cover the active sites of the catalyst, decreasing its efficiency. Hence, to prevent S poison, a desulfurization step is added as the first process before the reaction with steam begins.[27] A support material (usually magnesium and aluminum spinel, MgAl2O4, or α-alumina) is used as support for Ni in the SMR process to prevent carbon formation on the active sites.[28]

Catalysts based on Co,[31,34] noble metals,[31,34] Ru,[35] and Rh[36] are also used in SMR. However, the high cost of these metals is the main drawback for large-scale use. In some cases, a small percent of noble metal can be added to enhance the catalytic activity of Ni-based materials. From an economical point of view, the production costs per kg of H2 in the SMR using Ni catalyst can reach about US$ 2.08 when the carbon capture and storage (CCS) process is not included. On the other hand, these costs can up to US$2.27 kg−1H2−1 when CCS is applied, which reduces the environmental damage and still keeps the process economically competitive.[4,29] SMR is a process classified as gray hydrogen, and this way must be replaced by more sustainable processes in the next 30 years. The integration of SMR with CCS strategy changes the color code of the H2 produced from gray to blue, and it is an important starting point for decarbonization for HPP.

3.2. Partial Oxidation Process

The partial oxidation process (POxP) is an attractive and cheaper alternative for H2 production, because it minimizes large amounts of expensive superheated steam.[37] POxP basically involves the conversion of steam (H2O), O2, and different hydrocarbons into H2 and CO (Equation (3)-(5)).[29] An important feature of this method is that heavier feedstocks, such as oil residues and even coal (gasification process), can be used, and this gives it a wide range of feedstock possibilities. Despite heavier oil fractions requests desulfurization, which increase costs, the overall process exhibits a competitive economic price.

\[
\text{C}_m\text{H}_n + n\text{H}_2\text{O} \rightarrow n\text{CO} + \left( n + \frac{1}{2}m \right)\text{H}_2 \tag{3}
\]

\[
\text{C}_m\text{H}_n + \frac{1}{2}n\text{O}_2 + \frac{1}{2}n\text{H}_2\tag{4}
\]

\[
\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2; \quad \Delta H_{298K}^0 = -36.0 \text{ kJ mol}^{-1} \tag{5}
\]

POxP is performed at elevated temperatures and high pressures, and the understanding of the mechanisms reactions still remains a challenge.[38–39] An important dilemma emerges from this point, where the question is putting effort to study POxP and improve the process or change the focus to green hydrogen. Two reaction mechanisms have been proposed.[40,41] In the combustion and reforming reaction (CRR), the methane, for example, reacts with O2 (first step) generating CO2 and H2O. The remaining CH4 reacts with steam and CO2 by typical SMR and dry reforming processes, respectively, giving rise to a CO/H2 mixture that will be further separated. In the direct partial oxidation (DPO) where the mixture CO/H2 is formed in a single step via CH4 + 1/2O2 → CO + 2H2. In addition, catalysts are needed to improve the process, turning it faster and more effective. They are usually made of group-VII noble metals, such as Rh, Pt, Pd, Ir, and Ru, and non-noble metals, such as Ni and Co.[32–44] The conversion of CO with steam in a typical WGS reaction, hence, complements the process generating more H2 and also CO2.

From the carbon emissions point of view, POxP is classified as gray, because a large amount of CO2 is generated by the end of the process. However, if the CCS approach is used, the POxP color code can change from gray to blue. On the other hand, the POxP using coal can be named gasification process, and it is the worst way to produce H2 in terms of pollution, and because of this, the H2 produced by this industry is labeled as brown or black hydrogen.

3.3. Autothermal Reforming

When partial oxidation and steam reforming are combined in the same reactor, a new route to produce hydrogen gas is founded, and the process is known as autothermal reforming (ATR).[45] In this system, the partial oxidation step generates the heat amount that will be consumed later on the steam reforming process, and the overall procedure is thermally neutral. When a general hydrocarbon is used, the following reaction takes place

\[
\text{C}_m\text{H}_n + \frac{1}{2}m\text{H}_2\text{O} + \frac{1}{4}m\text{O}_2 \rightarrow m\text{CO} + \left( \frac{1}{2}m + \frac{1}{2}n \right)\text{H}_2; \quad \Delta H^0 \approx 0 \tag{6}
\]

As shown, the syngas is produced; however, the practical advantage of ATR is the combination of low-temperature operation conditions prevent from partial oxidation and the high hydrogen/carbon ratio from the SMR process.[46] Furthermore, ATR is usually used for generating hydrogen on a smaller scale.[47,48] The catalyst for ATR must be compatible with SMR and partial oxidation reactions, which is a real challenge. In addition, its selection should consider the fuel used, and there are two ways in which this process can occur, either using the same catalyst or using one catalyst for SMR reaction and another for partial oxidation step.[37,49] For fuels with lower molecular weight, a Cu-based catalyst is generally used, and for heavier hydrocarbons, Pt, Rh, and Ru catalysts or ion conduction ceria supported non-noble metal formulation, such as Fe, Co, and Ni, are used.[47]

ATR is also classified as gray hydrogen because of the CO2 emissions. Over again, the introduction of the CCS approach can change its classification to blue.

3.4. Methane Pyrolysis

Besides the previously discussed processes, another way that could be used to produce H2 is methane pyrolysis. In this
procedure, also called methane decomposition, thermal treatment is applied to convert natural gas into \( H_2 \) and \( C \) without \( \text{CO}_2 \) emissions.\(^{[7]}\) The endothermic reaction is described as follows:

\[
\text{CH}_4(g) \xrightarrow{\Delta} \text{C}(s) + 2\text{H}_2(g) \quad \Delta H^\circ_R = 74.85 \text{ kJ mol}^{-1}
\]  

(7)

The solid carbon produced avoids the \( \text{CO}_2 \) emission and can be transported and stored permanently, which decreases the overall cost, because \( \text{CO}_2 \) sequestration units are absent in the system. Furthermore, the produced carbon may have some value for further purposes, such as color pigments or tires.\(^{[50,51]}\) As a thermal input is necessary, methane pyrolysis is usually performed at high temperatures to reach a homogeneous reaction rate. In a view of that, the main drawback for this technique is the widely known coke formation, which occurs in the tubular reactor walls and may deactivate the catalyst,\(^{[50,51,53]}\) such as supported metals or oxides.

In terms of carbon emission, the methane pyrolysis for \( H_2 \) production is classified as turquoise (see Figure 2). This color represents a cleaner process than the others based on FFs. Nevertheless, the cleanliness of the process depends on the energy input, because the energy produced from renewable generates low environmental impact processes.

4. Hydrogen from Water

4.1. Electrolysis of Water

The search for clean, renewable, and environmentally friendly hydrogen sources has made water an excellent feedstock candidate to produce hydrogen.\(^{[1,29]}\) The production of clean \( H_2 \) from water occurs by a system known as WS, which in its simplest form uses an electrical current passing through two electrodes to complete the endergonic hydrolysis of water into hydrogen and oxygen. The overall process consists of two half-reactions, in which the anodic process is called oxygen evolution reaction (OER), where the water oxidation reaction (WOR) takes place, and the cathodic process is known as hydrogen evolution reaction (HER), where the hydrogen gas is produced, as it is shown in the following reactions at \( \text{pH} = 0 \).\(^{[12,54-56]}\)

**Anodic Process:** \( 2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(aq) + 4\text{H}^+(aq) + 4\text{e}^- \quad V_{\text{an}} = 1.23 \text{V versus reversible hydrogen electrode (RHE)} \)

(8)

**Cathodic Process:** \( 4\text{H}^+(aq) + 4\text{e}^- \rightarrow 2\text{H}_2(g) \quad V_{\text{cat}} = 0.00 \text{V versus RHE} \)

(9)

**Global Process:** \( 2\text{H}_2\text{O}(l) \rightarrow 2\text{O}_2(aq) + 2\text{H}_2(g) \quad V_{\text{eq}} = 1.23 \text{V versus RHE} \)

(10)

The great limitation for hydrogen production through this process resides in the anodic reaction, where the oxygen evolution (water oxidation) takes place, which is the most energy-intensive and kinetically slow step in the overall WS process. The water oxidation process to oxygen implicates a complex electronic transfer involving four electrons and four protons.\(^{[57]}\) Therefore, the WS is either kinetic or thermodynamic unfavorable, and in ideal conditions, a potential of 1.23 V (\( V_{\text{equilibrium}} \)) must be applied to the system to start the process. In addition, efficient and stable catalysts are required to decrease the overpotential of the reaction, and an external energy source, such as electricity (electrolysis) or solar (photocatalysis), must be used.\(^{[58,59]}\)

The system where electrolysis of water takes place is known as electrolyzer, which basically consists of a cathode and an anode separated by a membrane immersed in an electrolyte. So far, three main electrolysis cells are used and studied: alkaline electrolysis cells (AECs), proton exchange membrane electrolysis cells (PEMECs), and solid oxide electrolysis cells (SOECs).\(^{[60]}\) Figure 3 shows these cells’ setup and their main differences.

AEC has been widely used for industrial and large-scale applications since 1920, being already available, stable, and exhibiting a considerable low capital cost (around USA$ 1180 kW\(^{-1} \)).\(^{[61]}\) In addition, this cell was shown to operate for over 55 k hours, proving itself to be very stable, which is very important for its large-scale application. However, one of the main drawbacks for this cell is its low current density (<0.45 A cm\(^{-2} \)) and high cell voltage (1.8–2.4 V),\(^{[62–64]}\) which can increase the cost for hydrogen production. Thus, some developments need to be done to make a more suitable cell, with a significantly lower cost, which is still three times more expensive than steam reforming processes.\(^{[60,62,65,66]}\)

![Figure 3. Main electrolysis cells technologies setup. They can be classified as: AECs, PEMECs, and SOECs.\(^{[60]}\)](image-url)
PEMECs are based on a solid polymer electrolyte. They were developed in 1960 as an attempt to overcome the problems presented by the AECs, and after considerable effort in research and improvements, PEMEC has been reported a milestone in the electrolyzer field.[66,67]

Membranes are the cornerstone for the PEMEC, and they are responsible for separating product gases, transporting protons, and supporting the cathode and anode catalyst layer. The most used membranes are based on a perfluorosulfonic acid polymer, such as Nafion, Fumapem, Flemion, and Aciplex.[62] Although all the beforehand cited polymers present great advantages for membrane applications, Nafion is the one that is usually used, due to its excellent chemical and thermal stability, mechanical strength, high durability, high proton conductivity, and the fact that it can operate at high current densities.[62,68,69] However, one of the main drawbacks of the use of Nafion is its disposal, which can be very expensive due to the presence of fluorine in the structure. Thus, alternative membranes have been studied, yet they present low current densities and low durability, which make them unviable.[62,70]

Even in the same cell voltage as AECs, PEMECs present higher current density (1.0–2.0 A cm\(^{-2}\)), efficiency, and great stability, operating for over 60 k h, being able to produce pure hydrogen. However, the main catalysts are made of noble metals, which increases the capital cost (around US$2300 kW\(^{-1}\)).[63,64] The system also requires pure water, which limits its application. Hence, studies have been made trying to reduce the system complexity and its cost, aiming to find less expensive materials.[61,66,70]

SOEC is a more recently developed cell, and it is not widely commercialized, because the system has been demonstrated to work only on laboratory scales. The cell uses solid ion-conducting ceramics as the electrolyte, which allows it to operate at higher temperatures (900–1000 °C).[67] These cells have high electrical efficiency, moderate current densities (0.3–1.0 A cm\(^{-2}\)), operate at lower cell voltage (0.98–1.3 V),[63,64] low material cost, and also the option to operate in reverse mode as a FC or in co-electrolysis mode. Nonetheless, the high-temperature operation can cause material degradation, which is a huge drawback and elevates the capital cost (higher than US$2400 kW\(^{-1}\)). Therefore, the research in this area is focused on the development of catalyst materials that can withstand high temperatures, further making it commercially viable.[61,66,67,71]

Nevertheless, it is worth mentioning that all these data presented for the electrolyzers are directly dependent on the stack level in the cells, which have an impact on the cells performance, efficiency, and stability; therefore, it is an important parameter to be considered in the study of better systems for water electrolysis.[66]

In overall WS electrochemical system, the actual operational voltage (\(V_{\text{op}}\)) is different than \(V_{\text{eq}}\), because it depends on the reaction’s kinetics and on the cell design, being represented by the following equation

\[
V_{\text{op}} = V_{\text{eq}} + \eta_\alpha + |\eta_\text{C}| + \eta_\text{IR}
\]  

(11)

where \(\eta_\alpha\) and \(\eta_\text{C}\) are the overpotential for the anodic (OER) and cathodic (HER) reactions, respectively, and \(\eta_\text{IR}\) is the additional overpotential required to compensate for resistance losses within the cell.[58] In an ideal system, \(\eta_\alpha\) and \(\eta_\text{C}\) would be close to zero, and \(V_{\text{op}}\) would depend only on \(\eta_\text{IR}\), which could be minimized by the cell design. Nonetheless, this is not what happens in reality, in which the reactions face a very high activation energy barrier due to the kinetics limitations, increasing the overpotential that needs to be overcome.[72] The system can become even more complex for photocatalysis, where semiconductor materials are incorporated into the electrode in a way that the solar energy is directly harvested, requiring more mechanistic steps and lowering the overall production efficiency, as it will be discussed further in Section 4.2.[57] Thus, the research in water electrolysis processes focuses on approaches to reduce this overpotential by improving electrodes, electrolytes, and catalysts, trying to unravel ways to boost reaction kinetics.[55,59,73–76]

Among the numerous catalysts that have been studied, Ru, Ir, and their respective oxides stood out as the state of the art for WOR, presenting the best electrocatalytic activities toward OER in both acidic and alkaline solution.[77] Ir, Ru, and their respective oxides act as water oxidation catalysts are ordered in the following sequence: Ru > Ir ≈ RuO\(_2\) > IrO\(_2\). The overpotential needed to achieve a current density of 5.0 mA cm\(^{-2}\) is 300 and 400 mV for RuO\(_2\) and IrO\(_2\), respectively.[78] Even though both oxides have a good performance and activity during water oxidation, their main drawbacks are their low stability and high cost.[79]

The state-of-the-art catalysts for the HER are based on Pt, which is found to be an efficient electrocatalyst, exhibiting a near to zero overpotential and high current densities.[56,80] Pt-based catalysts present an overpotential of 0.05 V in acidic media and are able to keep the same value even after 2 h of reaction. At an overpotential of 0.1 V, they are also able to achieve the current densities of 110 ± 70 and 220 ± 80 mA cm\(^{-2}\) for two different studies with platinum electrodes, with differences in the electrolytes.[55,81]

Even though these catalysts are considered as the state of the art for WS, their high cost and scarcity create a huge obstacle to their large-scale application. Hence, the development of catalysts for HER and OER should be efficient, stable, cheap, operate at low overpotential, and based on earth-abundant elements. This is crucial to a suitable hydrogen generation through WS. In a view of that, an enormous amount of effort, both theoretical and experimental, has been put into the development of different catalysts based on earth-abundant transition metals, especially from the first transition row (e.g., Co, Fe, Ni, Cu, Mn, Cr, and Zn) as an attempt of substituting noble metals catalysts, making the WS an economically viable process for the hydrogen production.[54–56,59,75,76,82–86] Jaramillo and co-workers[55] published a study comparing the main catalyst for both OER and HER, working in alkaline and acid medium. In this article, the authors present a benchmarking for these catalysts, showing how the activity of earth-abundant catalysts can be compared with the one from noble metals, demonstrating the main features that need to be improved for the development of suitable non-noble metal catalysts.

Even though a huge amount of research has been made in this area, the use of earth-abundant catalysts is still limited by their low activity and, most of the time, stability, which inhibit their applications for large-scale hydrogen production.[12,35,36]
Based on the development of the WS technology so far, the cost per kg of hydrogen is in the range of US$ 7.98–8.40 for electrolysis with an efficiency of up to 60% and is about US$ 10.36 kg⁻¹ for the photocatalysis, and the efficiency up to 12%, which makes the electrolysis a better option for the WS. Nonetheless, this system is still too expensive, and the costs need to be reduced to be competitive with the gray hydrogen (steam reforming, for example).[10,12,18,87]

Nonetheless, it is important to highlight that the WS process can only be considered as a good and eco-friendly alternative for green H₂ production if the input energy in the electrolyzer is being supplied from RE sources; otherwise, this system would not produce a 100% green and clean hydrogen.[13,88]

Pink hydrogen has been considered as an alternative with a low-carbon emission in the hydrogen production process, because the input energy comes from nuclear energy reactors. In these systems, nuclear electricity can be directly used in an electrolysis unit for hydrogen production.[89,90] Therefore, electrolyzers can be built inside or close to the nuclear plants, to facilitate an in-site H₂ production.[15,91] The hydrogen can then be transported in pipelines for other applications or be transferred to an FC for electricity generation, which would be further transferred into the grid.

Nuclear electricity has zero-carbon emission, and because of this, some governments are trying to implement the use of this technology. However, the main drawback is that nuclear plants have a high risk of catastrophic consequences. In addition, nuclear waste is very dangerous, and its disposal and treatment are expensive, which can make its use not suitable.[6,13,89–91]

In the search for renewable and safer energy sources, wind is very important, being clean, renewable, and low cost. In addition, it can bring outstanding benefits for regions and countries with great wind conditions.[92,93] One of the great challenges for wind power utilization is that the wind-power plants are usually installed in locations far from regions with high electricity consumption, resulting in long-distance transmission and high-power losses.

Thus, the exploration of local use of wind power has been considered, and the utilization for local green H₂ production using electrolyzers would be a great opportunity.[94–95] In this case, H₂ can be produced via a water electrolysis system, which its energy input is supplied by a wind turbine. If necessary and during periods with no wind, the power needed to produce the hydrogen could be withdrawn from the grid. The H₂ produced through electrolyzers using a combination of RE and non-RE is classified as yellow hydrogen.[96] Nevertheless, the greatest challenge for a wind-power utilization for water electrolysis is that, sometimes, the wind-to-power conversion is not efficient; thus, the power would not be enough to supply the electrolyzer’s requirements.[93–95] To overcome this challenge, wind-power farms are usually installed close to the ocean or in other regions with constant and high velocities of wind. In addition, other studies try to improve the wind-power systems to increase their efficiency; also, the electrolyzer can be adapted to work better with the power supplied by wind-power systems.[92–96]

4.2. Sunlight to Produce H₂

Solar energy is inexhaustible, clean, and the most abundant energy resource on Earth, providing in 1 h (4.3 × 10²⁰ J) more energy than the global annual energy consumption, 4.1 × 10²⁰ J.[97] Among the strategies to produce green hydrogen from water electrolysis using sunlight, two approaches have received great attention and will be discussed as follows. The first one is the direct conversion of solar energy to hydrogen in a photoelectrochemical (PEC) cell. In the latter, an electrolyzer is powered by a photovoltaic (PV) cell, and the systems can operate independently.[93,98]

The first PEC cell was proposed by Fujishima and Honda in 1972[99] and was composed of an n-type TiO₂ photoanode and a Pt cathode, as shown in Figure 4. As the energy of the incident radiation is higher than the bandgap of the semiconductor (TiO₂), electrons (e⁻) are photoexcited to the conduction band (CB), leaving holes (h⁺) in the valence band (VB). The photogenerated electrons flow to the Pt electrode through an external circuit to promote HER. At the same time, water oxidation by the holes occurs on the semiconductor surface. The HER takes place when CB potential is more negative than 0 V versus normal hydrogen electrode (NHE) (H⁺ /H₂ redox potential), and the OER is accomplished if the VB potential of the photocatalyst is larger than 1.23 eV (at pH = 0), the minimum Gibbs free energy requirement for WS (Equation (10)).

The efficiency of the PEC cell depends on the light-harvesting capability of the semiconductor; e.g., the large bandgap of TiO₂ (3.2 eV in anatase phase) restrains its application to absorption of UV light, which corresponds to only 4% of the solar spectrum. In this sense, the modification of the electronic band structure of the semiconductors by doping has been proposed to extend the light absorption to the visible light region. Furthermore, semiconductors with a narrow bandgap, such as WO₃, BiVO₄, Fe₂O₃, and CdS can be used as alternatives to TiO₂.[100–102]

Besides the photon absorption and exciton generation, the dynamics of the electrons and holes, including trapping, recombination, and interfacial transfer, can also affect the PEC performance of semiconductors.[103] and a strong dependency on the crystal structure, the presence of defects, size, and conductivity of the photocatalyst has been observed.

Furthermore, many efforts have been devoted to developing heterojunction systems, which consists of coupling two or more semiconductors and where electrons and holes can be spatially separated, minimizing the recombination. Several heterojunction configurations were reviewed and discussed in detail by Tang and co-workers.[104,105]

A promising configuration, inspired on the Z-scheme of the photosynthetic system of green plants, could meet the requirements for the efficient hydrogen production from solar-driven WS. In this mimicking system (Figure 4), two photocatalysts with small bandgap can harvest a wide range of the solar spectrum. Considering that the OER and the HER take place in the isolated photoanode and photocathode, respectively, photocatalysts that are active for only a half-reaction can be used. Water oxidation and reduction co-catalysts (WOC and WRC) can be attached to the electrodes to improve the PEC performance. Moreover, in the Z-scheme, a redox mediator is used in transportation electrons, allowing an efficient charge separation, suppressing the e⁻ / h⁺ recombination.[106] The strategies inspired in nature are challengeable but still are a promising alternative. Researchers from all over the world have worked hard in the past decades to improve efficiency and the costs of the hydrogen produced from a PEC, but this strategy is out of commercial applications.
In this regard, according to Grimm et al.,\textsuperscript{[107]} the PV-electrolysis system can be more competitive than the PEC devices. In a PV system, the electrolyzer’s energy input is supplied by PV devices that are connected to each other. In a PV-electrolysis system, the solar panels capture solar light and transport the energy, usually via wires, to a separate electrolyzer.\textsuperscript{[107–109]} These systems can be typically either directly coupled or connected via a converter. However, the modeling tool for PV electrolysis, regarding the integration and coupling of the subsystems as well as the modeling approach for the solar cell device, has a direct impact on the system efficiency toward H\textsubscript{2} production.\textsuperscript{[107,110,111]} The greatest challenge faced by the development of these coupled devices is the achievement of high solar-to-hydrogen (STH) efficiencies, due to a limitation to solar energy conversion. The improvement of STH efficiencies can be a significant driving force for reducing the H\textsubscript{2} generation cost.\textsuperscript{[55,98,112]} Thus, some changes and improvements need to be done to the system to make it suitable. Using a multijunction solar cell with two electrolyzers in series, researchers found an effective way to minimize the excessive voltage generated by a multijunction solar cell, allowing greater utilization of the high-efficiency PV for WS, achieving an STH efficiency of over 30\%.\textsuperscript{[98]} Nonetheless, these prototypes still need to be improved and adapted in a way to reduce the cost of H\textsubscript{2} and make the use of electrolyzers commercially suitable.\textsuperscript{[98,107–109,111–113]}

5. Sources of Water
5.1. Hydrogen from Wastewater

The use of wastewater as a feedstock for the WS process can provide on-site treatment for water recycling and reuse, along with the production of hydrogen. These features offer great advantages regarding the use of water, because the resources are not equally distributed around the world, besides, due to the population growth, they are on the edge of an emerging crisis. According to the World Health Organization, around 2.2 billion people do not have safely managed drink water. In addition, 4.2 billion people do not have safely managed sanitation services, and 3 billion lack basic hand-washing facilities.\textsuperscript{[114,115]} The poor water quality exposes these people to several diseases, which may also result in death.\textsuperscript{[116]}

In face of this scenario, the use of wastewater is a great alternative and excellent opportunity for the obtention of clean water and energy storage (H\textsubscript{2}).\textsuperscript{[117]} Each year, about 310 km\textsuperscript{3} (310 \times 10\textsuperscript{12} L) of municipal wastewater is produced around the world, and part of this amount (around 70\%) is treated by conventional methods and reused for different approaches. This great supply of wastewater can be used as an alternative feedstock for WS, which would present another way to treat this water and make it clean and being able to be reused. In addition, energy, in form of hydrogen, could be produced and stored,
displaying an incredible opportunity, especially for communities where water is a scarce resource.\textsuperscript{[118–121]}

When wastewater is used as a feedstock, H\textsubscript{2} can be produced using microbial electrolysis cells (MECs) or wastewater electrolysis cells (WECs), MECs utilize microbes at the anode to convert biodegradable substrates, such as organic matter, into electrical current and protons (H\textsuperscript{+}). The electrons are transferred to the cathode, so the protons can be reduced into hydrogen gas.\textsuperscript{[122,123]} These cells are based on the use of microbes to degrade pollutants, making the MECs part of the microbiological pathway for hydrogen production. Nevertheless, there are metabolic cells that can oxidize the organic matter present in wastewater, without using microbes, known as WEC.

The WEC works in a similar way to the MECs, and the organic and inorganic matter are oxidized in the anode at the same time that WOR takes place, producing electrons (electrical current) and H\textsuperscript{+}. Then, the electrons migrate to the cathode where hydrogen is produced by the reduction of protons.\textsuperscript{[124]} In this system, usually powered by PV cells, the organic pollutants can be eliminated through a direct or indirect process.\textsuperscript{[125]} During the H\textsubscript{2}O oxidation to O\textsubscript{2}, some intermediates are formed (reactive oxygen species [ROS]). These ROS can be used for the direct oxidation of contaminants and pollutants. ROS can also react with chloride existent in wastewater and produce reactive chlorine species (RCS) and chlorine radicals, which will lead to indirect oxidation of organic and inorganic matter.\textsuperscript{[119–121]}

As the aforementioned reactions are totally dependent on ROS formation, the anode composition is a determining factor for wastewater electrolysis and purification.\textsuperscript{[126,127]} In addition, the wastewater matrix is very complex, and various side reactions that happen during the electrochemical process may interfere (being benefic or malefic) directly with the H\textsubscript{2} generation efficiency. In this context, the current and energy conversion efficiency for hydrogen generation is around 40–80\% and 30–60\%, respectively.\textsuperscript{[124]}

As aforementioned, the WEC can certainly have the potential of becoming the future technology for on-site wastewater treatment, coupled with water reuse and energy storage, in the form of H\textsubscript{2}. In addition, a scaled-up prototype could easily be installed in various environments, such as urban and rural areas, offering great opportunities especially for remote locations, where they face a lack of sanitation facilities, not being able to treat the local wastewater. Besides that, these cells can also be used to treat industrial wastewater and landfill leachate, also contributing to the development of alternative methods for decentralized H\textsubscript{2} production.

The use of wastewater to produce hydrogen also opens opportunities for producing hydrogen using microorganisms, commonly known as biohydrogen production, in which waste can act as the substrate, and will be discussed in detail in Section 5.1.2.

5.1.1. Biohydrogen

The utilization of biohydrogen has been attracting researchers’ attention, mainly because it is a carbon-free emission route for hydrogen production. This route could be classified as a strategy to produce white hydrogen as discussed previously. In addition, it allows the use of waste as a substrate, which also contributes to waste degradation and treatment, coupled with energy generation, in the form of molecular H\textsubscript{2}. Besides being eco-friendly and carbon-free, biohydrogen has the advantage of being able to use a wide range of substrates to produce hydrogen, from biomass, to different types of organic wastes, which increases the range of applications for biohydrogen production.\textsuperscript{[128–130]}

The fundamental basis of microbial H\textsubscript{2} production is that the microorganisms act as the catalysts for the reaction, forasmuch as they can use redox reactions to obtain hydrogen. In general, they use protons (H\textsuperscript{+}) and electrons (e\textsuperscript{–}) that are generated in some internal enzyme’s reaction, to combine and form H\textsubscript{2}, as it is shown in the following equation.\textsuperscript{[128,131]}

\[
4H^+ + 4e^- \rightarrow 2H_2 \tag{12}
\]

The different processes of biohydrogen production will change in terms of electron donor types, redox potentials, the substrate type, and the microorganism that will be responsible for carrying out the overall processes. Hence, the biohydrogen production routes are separated into two different classes: fermentation, which can be dark or photo-process, and photosynthesis, which can be a direct or indirect pathway. These processes will be briefly discussed subsequently, and Table 1 summarizes the main advantage and disadvantage for each process.\textsuperscript{[128,131–133]}

\textbf{Direct Biophotolysis:} Direct biophotolysis for biohydrogen production is based on the photosynthesis system, a complex redox process that can be accomplished during the metabolic cycle in green algae and plants cells.\textsuperscript{[128,134]} In this process, a microbial photosynthesis mechanism uses solar energy to convert a water molecule into molecular hydrogen and oxygen, being a combination of biological and chemical processes. During the mechanism, photosystem I (PSI) and photosystem II (PSII) play an important part in the H\textsubscript{2} production process. PSII is responsible for splitting water molecules into two protons and oxygen, whereas PSI is involved in the reduction of CO\textsubscript{2}.\textsuperscript{[128,135–137]} Thus, hydrogen can be formed by the presence of hydrogenase or by CO\textsubscript{2} reduction by PSI.\textsuperscript{[136,137]}

\textbf{Indirect Biophotolysis:} Indirect biophotolysis was developed to overcome the hydrogenase enzyme sensibility to oxygen, and in this process, hydrogen can be produced by microalgae (green algae) and cyanobacteria from starch or glycogen.\textsuperscript{[138–140]} During the mechanism, two main steps are involved; first, a carbohydrate is formed using light energy, and then, H\textsubscript{2} is produced from the synthesized carbohydrate through the cell’s metabolism, operating under dark conditions. Contrary to the direct process, during the indirect biophotolysis, adenosine triphosphate (ATP) needs to be formed and is an important part of the H\textsubscript{2} production.\textsuperscript{[128,134,139]}

After using the available O\textsubscript{2}, the cells can undergo anaerobic condition, which can facilitate the hydrogenase enzyme functionalization and activity, because this enzyme is extremely oxygen sensible. This process is dependent on environmental factors, such as light intensity, carbon sources, and degree of anaerobiosis.\textsuperscript{[128,135,138]}

Although the use of direct and indirect biophotolysis is promising, it has a low hydrogen yield, and the complex photosynthesis system difficulties make some changes that would enhance efficiency. Therefore, fermentation systems have been receiving
more attention, because they are simpler and present a higher yield of hydrogen.

**Dark Fermentation**: Dark fermentation is the fermentative conversion of organic substrates to produce biogas, which takes place in anaerobic conditions and without the presence of light. In this process, obligate anaerobes and facultative organisms consume complex carbohydrates and a large number of organic acids as by-products, which will need to be further removed to increase the H₂ purity. In addition, some of the by-products can be toxic, which might increase the cost of purification and treatment. Although it has a relatively high yield, the yield of H₂ per substrate consumed (Y₁(H₂/S)) is limited by metabolic constraints of dark fermentative microorganisms, following the theoretical limit, known as “Thauer limit.” Thus, these systems still present some drawbacks that need to be overcome to make it more suitable.[144]

**Photo-Fermentation**: Photo-fermentation is a process in which a photosynthetic microorganism uses light (sun or artificial) and consumes reducing sugars and organic acids, producing hydrogen.[133,141,143] During the mechanism, the electrons from water molecules are used for a photochemical oxidation by PSII, and these electrons are utilized by [Fe]-hydrogenase in the direct biophotolysis method, leading to the photosynthetic hydrogen production. The greatest advantage is that it can use a wide range of substrates, including organic acids, organic acid-rich wastewater, or organic acid-rich biomass. In addition, some factors such as intensity and wavelength of light influence directly in the biogas production in this system.[128,133,140,141] The overall reaction involved in the process, along with the advantages and disadvantages of this process, is shown in Table 1.

| Process               | Advantages                                           | Disadvantages                                           | Reaction                                          |
|-----------------------|------------------------------------------------------|---------------------------------------------------------|--------------------------------------------------|
| Dark fermentation     | • High H₂ evolution rates (HERs)                     | • The yield of H₂ is limited by metabolic constraints   | C₂H₅O₄ + 2H₂O →                                    |
|                       | • Simple operation limits                            | • Production of toxic compounds                         | 2CH₃COOH + 4H₂ + 2CO₂                              |
|                       | • Low energy requirements                           |                                                         |                                                  |
|                       | • Does not depend on O₂ (anaerobic process)          |                                                         |                                                  |
|                       | • Wide range of substrates available                 |                                                         |                                                  |
| Photo-fermentation    | • Wide range of substrates available                 | • Requires constant light source for photosynthesis,    | N₂ + 8 H⁺ + 8 e⁻ + 16 ATP →                       |
|                       | • High H₂ production yield                          | making it expensive                                     | 2NH₃ + H₂ + 16 ADP + 16 Pi                        |
|                       | • It has no activity for O₂ evolution               | • Low solar light conversion                           |                                                  |
| Direct biophotolysis  | • Simpler                                           | • Sensitivity of hydrogenase for O₂                    | 2 H₂O + solar energy →                            |
|                       | • High theoretical efficiency                        | • Low efficiency                                        | 2 H₂ + O₂                                         |
|                       | • Produces H₂ from H₂O                              | • Low light conversion                                  |                                                  |
|                       | • It is not necessary to produce ATP                 |                                                         |                                                  |
|                       | • Solar energy                                       |                                                         |                                                  |
| Indirect biophotolysis| • Produce hydrogen from water                        | • Light dependent                                       | C₂H₅O₄ + 6H₂O + solar energy                      |
|                       | • Microorganisms grow in environments               | • Needs ATP                                             | → 6CO₂ + 12 H₂                                     |
|                       | containing simple minerals                           | • High energy cost                                       |                                                  |
|                       |                                                       | • Enzyme limitation by O₂                               |                                                  |
|                       |                                                       | • Low production rate                                    |                                                  |

Table 1. Comparison between the processes for biohydrogen production.

5.2. Hydrogen from Seawater

The use of seawater as the WS feedstock for hydrogen production can also bring incredible advantages for different communities around the globe. As it is common knowledge, 70% of the Earth’s surface is covered by water; thus, it is possible to state that water is the most abundant natural resource on the planet. In addition, considering the water reserves, the oceans represent 96.5% of them, containing approximately a total of 1.35 10³² L of seawater with a fairly homogeneous geographic distribution.[145,146] The use of seawater instead of freshwater can facilitate the implementation of PV-powered electrolyzers in some remote and arid areas where this resource is scarce or its use for energy production (WS) would bring some harm to the local reserve.[147]

The world’s arid desert regions are mainly located in the Middle East, South Africa, the west coast of the Americas, Australia, and the west of China, with a large area of it being located near ocean coastlines. All in all, Coastal Arid zones would present a great opportunity for the H₂ production from seawater, forasmuch as these regions have limited access to freshwater yet plenty access to seawater.[146,147] In addition, these areas have a high incidence of solar light most of the time throughout the year, which can favor the use of PV-powered water electrolysis systems and FCs, as this will not only provide a way of producing and storing energy (in the form of H₂), but will also allow the obtention of fresh drinking water from seawater.[98,147]
Seawater follows the same principles and reactions as when fresh water is used (reactions (9)-(11)). However, the huge amount of dissolved ions can be considered as the biggest drawback, considering that they can affect the catalytic system by decreasing its efficiency or causing some kind of degeneration to the electrodes.\[146,147\] Seawater is composed mainly by Na\(^+\), representing almost 42% of the total amount (0.486 mol kg\(^{-1}\)H\(_2\)O) and Cl\(^-\), which represents 49% of the total composition (0.565 mol gg\(^{-1}\)H\(_2\)O). Even though the other ions can also interfere and compete with the WOR, they are present in such a small amount that their effect can be neglected.\[148\] However, it is important to highlight that this is a general composition, and it can change in different locations.

The biggest challenge for splitting the seawater is that the presence of the ion chloride (Cl\(^-\)), in acid conditions, can lead to the anodic chlorine evolution reaction (CIER), which competes with the OER (water oxidation) and produces undesired side products, such as molecular chlorine or chlorinated oxidants, as it is shown in the following equation.\[149\]

\[
2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \quad V = 1.36\text{V} \text{versus RHE} \tag{13}
\]

Even though, from a thermodynamical point of view, OER is favored over CIER, the chlorine evolution is a simpler two-electron reaction, involving only one intermediate. Thus, CIER has faster kinetics and can take place at lower overpotentials, which can make them the major anodic reaction in acid conditions.\[146,147\] In this case, OER was found to be dominant only at current densities below 1 mA cm\(^{-2}\) or at very high current densities where CIER currents reach the mass transfer limitation.\[149,150\] When working in alkaline conditions, the hypochlorite formation, as shown in Equation (10), should be considered.

\[
\text{Cl}^- + 2 \text{OH}^- \rightarrow \text{ClO}^- + \text{H}_2\text{O} + 2e^- \quad V = 1.72\text{V} - 0.059\text{pH} \tag{14}
\]

The hypochlorite formation is also a simple reaction involving two electrons, thus, kinetically favored over OER, even though OER is thermodynamically favored. In addition, the electrode potential for hypochlorite formation is pH-dependent, following the OER potential, as shown in the Pourbaix diagram (Figure 5).\[147\] As both standard potentials are parallel in the pH range from 7.5 to 14, it is possible to obtain a standard potential difference (\(E_{\text{ClER}} - E_{\text{OER}}\)) of 480 mV. Therefore, it can be stated that OER is favored at higher pH (\(\geq 7.5\)), provided that the overpotential required is at values lower than 480 mV, when hypochlorite formation is thermodynamically not allowed, and no other side reaction competes with the water oxidation.\[150\]

A similar standard potential difference cannot be obtained for OER and CIER, because this potential difference is considerably smaller, making it more difficult to achieve higher current densities at an overpotential where CIER is thermodynamically not allowed. Hence, carrying out seawater electrolysis in alkaline conditions presents more advantages.\[147,151\] Besides operating at a high pH, different approaches can be made to improve seawater electrolysis, such as the design and development of catalysts with active sites that favor the adsorption of OER intermediates, making them more selective. Furthermore, as an attempt of overcoming the thermodynamic overpotential limitations, Cl\(^-\) blocking layers can be added alongside the OER catalyst to avoid the diffusion of Cl\(^-\) ions from the electrolyte toward the anodic catalyst, which would improve the surface selectivity regarding OER.\[152\] Furthermore, the presence of Cl\(^-\) can bring corrosion problems, even in alkaline conditions; also, some insoluble precipitates can be formed on the surface of the electrodes, poisoning both OER and HER.\[153\]

Faced with the aforementioned challenges, seawater electrolysis requires a catalyst, for both anode and cathode, that is highly selective for the OER and HER reactions, and also resistant to corrosion and other degradations that can result from the ions composition. Thus, the catalyst design is fundamental for implementing a state-of-the-art seawater electrolysis technology.\[151–153\]

Figure 5. Pourbaix diagram for artificial seawater model. A chlorine system, in the case of dissolved 0.5 M NaCl aqueous solution and no other chlorine sources, with a total chlorine species (\(C_{\text{Cl},\text{tot}}\)) of 0.486 mol kg\(^{-1}\)H\(_2\)O. The electrode potential for OER is also included (assuming oxygen partial pressure of 0.21 atm = 0.021 MPa). Adapted with permission.\[147\] Copyright 2016, John Wiley and Sons.

For OER in alkaline pH, these catalysts are required to operate at an overpotential lower than 480 mV and at the current densities of at least 10 mA cm\(^{-2}\) to be considered as good candidates for commercial applications.\[147\] However, recent works have shown difficulties to achieve such high current densities at such low potentials especially in pH near to neutral (pH = 7 to 8) for seawater.\[152\]

Co-based catalysts have great research attention, being able to operate at high current densities and with high selectivity, even at overpotentials higher than 480 mV, where just a small amount of the total current is used to CIER.\[154,155\] Nonetheless, a lot of work is still required, so a better understanding regarding OER selectivity can be achieved and, thus, enhanced.\[152\]

Aiming to block Cl\(^-\) ions approximation, MnO\(_x\) protection overlays have been studied and presented themselves as an excellent opportunity. The studies showed that MnO\(_x\) was not involved in the OER mechanism, but acted as a Cl\(^-\) diffusion barrier, while remaining permeable to water so the OER could take place at the actual catalyst coated over the anode.\[152,156\]

Regarding the HER, the main challenge is not related to selectivity and faradaic efficiency; instead, they are related to species
that are presented in seawater composition that can poison the active sites, by blocking them. In addition, they can degrade and corrode the cathode catalyst. Therefore, studies are more focused on ways to increase the catalyst stability against corrosion and degradation and also on ways to create barriers that will avoid the deactivation on the catalyst surface.\cite{153,157}

Pt is known as the state-of-the-art catalyst for both alkaline and acid conditions; however, its high cost is the biggest drawback for its use, and new non-noble-based catalysts have been studied. Provided that, Ni or Ni-based metal alloys are usually used as HER catalysts due to their high performance and good stability.\cite{55} The use PEMEC could also bring great advantages, because the membranes could also work as a filtration barrier, protecting the cathode against deactivation. However, its configuration provides a minimal overpotential window that it is too good for the OER operation conditions aiming to avoid the CIER. Therefore, the study of catalysts that exhibit outstanding performance at a neutral to alkaline media can bring excellent opportunities for seawater splitting.\cite{122}

The efforts are focused on the mixing of Pt with a different metal (usually earth-abundant), aiming to maintain or increase their activity, but lowering the cost at the same time.\cite{146,150,152,158} Besides that, different earth-abundant-based catalysts have been studied, mainly involving transition metals of the first row. These metals can form complexes with different structures, ligands, and inorganic ions, making them very versatile, cheap, and easy to synthesize. Furthermore, they have been reported to achieve high current densities for seawater HER at low overpotentials, with high faradaic efficiencies for hydrogen production, which present them as a great opportunity for future large-scale seawater electrolysis cells.\cite{146,150,153,157,159} Another outstanding opportunity that has been extensively studied is the use of bifunctional catalysts, that can effectively operate as both the anode and cathode catalyst, making the cell design and construction easier and cheaper, with great operation conditions.\cite{85,146,150,153,160}

Although much effort is still required for the development of economically viable seawater electrolysis technology, all those foregoing mentioned catalysts have the potential of contributing to the development of robust and active catalysts that can use seawater as a feedstock for large-scale hydrogen production. In addition, using seawater electrolysis, some remote and arid areas that do not have access to fresh water can benefit from this feature, because this process can not only produce and store chemical energy but also presents the opportunity of obtaining fresh water directly from the ocean. Moreover, seawater is the most abundant natural resource on the planet, so its use presents remarkable energy opportunities for the near future.

6. Hydrogen Outside of the Earth

Although energy technologies still need to evolve and get more mature, it is important to reflect on some perspectives for the future of energy, considering matters like where it can be used the most in 100 years from now and what will be the energy demand then. All things considered, we dare to assume that the world and energy as we know it will not be the same, because life as we know is doomed to go through an imminent transformation that will change the planet in ways that cannot even be imagined. One of the biggest transformations that are expected for the near future is an increase in space exploration in different aspects, such as low-Earth orbit (LEO), high-Earth orbit (HEO), near-Earth asteroids (NEAs), Moon, Mars, and deep space missions.\cite{161–163}

However, one of the biggest challenges of these space missions is the systems for energy generation and storage technologies. Most of the limitations that are faced can be related to the systems durability, caused by low chemical reaction kinetics and efficiency, materials mechanical strength, environmental issues, and by the operating mode.\cite{161,163} Consequently, the development and expansion of new materials and technologies that can provide better energy generation and storage in space may bring enormous benefits for most of the space exploration goals, contributing to spacecraft, launch vehicles, landers, rovers, spacesuits, tools, habitats, communication networks, and basically anything that requires power and energy. Scientists argue that a breakthrough in power generation or energy storage can enable new space missions, bringing a rapid advance in the scientific understanding of outer planets and deep space.\cite{161,164}

Solar energy converted into electric energy through PV panels is undoubtedly the most important system of energy in space. However, another important alternative outside of the Earth is the FCs, which consists of an electrochemical cell that can convert the chemical energy of hydrogen and oxygen, directly into electricity, with high efficiency, durability, low cost, and with water as a side product.\cite{165,166} Both here and in space, the FCs can be used for stationary applications, in distributed power generation facilities, on both small and large scales. In addition, it can also be used for transportation vehicles, from personal motorcycles and small cars to buses, airplanes, and some spacecraft, creating the hydrogen fuel cell (FC) electric vehicle (HFCEV).\cite{167–169} These cells are designed to take the place of conventional internal combustion engine vehicles, being the main power source.\cite{168}

Regardless of the FCs drawbacks, related to power density and power response, they present great advantages and perspectives for future applications in space.\cite{170} In addition, electrolysis also produces O₂, which can be used for life support applications, helping to renew the oxygen for breathing supply in spacecraft and International Space Station (ISS).\cite{162} One of the great advantages of electrolysis and FCs utilization is that they can easily be adapted to scale and be used for in situ resource utilization (ISRU), where the cells are adapted into landers, rovers, spacesuits, and robots, producing electricity directly into them during the missions. For this reason, it is worth mentioning important that the systems have great durability and operate at high efficiency throughout the whole mission, which sometimes can take from days to years.\cite{161,162} In this context, PV cells can also be used as a power source for electrolysis, because sunlight incidence in space is enhanced. In addition, the sunlight energy capitalization needs to be carefully studied and designed, because it changes depending on the Sun’s distance and position.\cite{161,162}

Some agencies are already developing some regenerative FCs systems prototypes,\cite{171} that consists of a closed-loop system where water electrolysis takes place in a solar powered cell. Hydrogen and oxygen are then stored and fed later into a coupled FC, so electricity and heat can be produced. The water can be recycled and used again.\cite{172} One of the most recent
requirements, the use of 3D printing can bring outstanding advantages for both electrolysis and FC design, contributing to cheap, versatile, and robust materials. The main advantages for the use of 3D printing are the ability of fast prototyping, waste management, and generation of low-cost products. In addition, its use for space applications is extremely promising, because the parts can be printed and easily assembled directly in space, avoiding the costs of transporting materials from the Earth. According to Leach, it is estimated that the cost for transporting one ordinary brick to the moon can cost around two million dollars, which is unviable; however, as it was mentioned, 3D printing can overcome this. It is also possible to design and produce electrodes that can work both as the cathode and the anode at a very low price, which could be extremely beneficial to regenerative FC design, obtaining electrodes with a great efficiency toward O2 and H2 and an easy fabrication.

As H2 storage and transportation can be dangerous, technologies involving the storage of H2 in the form of ammonia (NH3) can bring benefits to space exploration and mainly to the chain of hydrogen on the Earth. NH3 can be easily and safely transported, and then, by a simple decomposition process, using heat and a catalyst can release N2 and H2 (mainly), spontaneously. Furthermore, there are some FCs that have been studied in which NH3 can be directly used and converted into power, which can be promising as well.

Even though the perspectives presented here still require massive research for the development of state-of-the-art technologies, the use of hydrogen energy in space is truly promising and has the potential of becoming the major energy source in the future, because the advantages presented by it are outstanding and can bring a rapid advance in the space exploration, providing a better scientific understanding of outer planets and deep space. The development of energetic strategies for space exploration requires high technology approach, which is also very sustainable, being able to inspire us here on the Earth to solve our problems.

7. Final Remarks and Challenges

7.1. Hydrogen Value Chain

The hydrogen chain (Figure 6) is complex and requires a detailed analysis. Hydrogen production processes might be a starting point for understanding the peculiarities and costs for the consumers. The feedstocks for H2 production change all processes and influence the prices and chain sustainability. FFSs are the most used feedstocks in the reforming processes, and this strategy represents about 95% of the H2 produced in the world. An important point to be featured is the implementation of a complicated step of carbon capture, utilization, and storage (CCUS), which can decrease the carbon emission; however, it increases the price. The electrolysis, on the other hand, uses water as feedstock and has zero-carbon emission, but depends on the energy input. Considering the use of water and RE input, the ideal scenario can be created. Therefore, the costs and the complex processes of WS must be considered before being
widely used or applied for a detailed plan in a sustainable future. Any choice has consequences, benefits, and challenges.

The purification of H2 is an important point, because its use depends on the purity level, and as a consequence, the prices are different. Reforming processes produce H2 with purity ranging from 87% to 94%, whereas electrolysis delivers H2 with purity superior to 99.9%. The purity requirement of the H2 for FC vehicles is grade 4.

Storing processes is also a challenge for the H2 economy, because it has a low volumetric energy density, which is a limitation. H2 can be stored in high-pressure vessels, in liquid form (high pressure and low temperature), adsorbed in high porous materials, or in liquid form as ammonia. Each strategy has an intrinsic cost and requires a specific transport. Local production can decrease transportation costs, but it requires investments for proper infrastructure. Logics costs for H2 transportation through road, rail, or maritime depend on the distance, suitable storage tanks, security, and laws. In addition, the key point in the hydrogen chain is the diversification of the industrial portfolio. Nowadays, H2 is mostly used in the petrochemical sector and agribusiness. The use of H2 as a clean fuel is still in early stages, with plenty of possibilities to explore and elucidate. The better understanding about the theme could bring new prospects in fine chemicals, steel, metallurgy, semiconductors, and other industries.

All aspects that have been discussed are relevant, but safety must be the key point for social recognition about the H2 importance. Both an essential feedstock for a sustainable industry and a safe product with a low risk of accidents are crucial.

Another important point to understand is how the chain, the costs, and the market are connected. The discussion about the hydrogen chain was previously made, and one of the biggest challenges of the companies is to estimate the final costs and sales price of the hydrogen. First of all, the costs of any product depend on countless factors and can be different according to the strategy, vision, and resources chosen by the companies. In general, the costs could be divided into Capex (capital expenditure) or Opex (operational expenditure), but the focus here is to call the attention of scientists and engineers to how difficult it is to calculate the price of hydrogen. No particular formula will be shown, but we will focus on the items that can be included in the H2 production cost calculation.

In terms of capital expense, some main elements must be considered, such as land, industrial machines, buildings, and system to storage. Operational costs must include some items as the process (feedstock, catalysts, purification, CCSU, and efficiency), industrial maintenance, energy input, transportation, legislation, safety, insurance, and so on. Other aspects to be highlighted are the market that uses the H2 (each market has a specific added value associated with the product), the scalability (the industrial scale changes all expenses), and the profit required (if it is considered the price to consumer). Each topic mentioned earlier could be described in detail and generates a great discussion. The sum, the particularity, the specific details, and the mathematical weighting of these items will generate the final price of hydrogen. The costs of H2, according to the process of production, are presented in Table 2. The idea of this table is to exemplify the prices and compare the production, efficiency, and cleanliness. Because of this, some fluctuation of values can be found.

### 7.2. Looking at 2050: Green Hydrogen and Zero-Emission Carbon

According to the International Energy Agency (IEA) in the document called “Net Zero by 2050,” published in May 2021,[183] humanity must reduce the global carbon emissions to net-zero by 2050. It is worth mentioning that the 26th Conference of the Parties (COP26) of the United Nations Framework Convention on Climate Change in November 2020 was an important moment for improving the global goals and action on climate based on the 2015 Paris Agreement. These efforts were defined to limit the long-term increase average of the global temperatures up to 1.5 °C. Some important characteristics are foreseen to 2050, as shown in Figure 7.

Strategic reports of specialized companies in the market for H2 have reported an estimation that the price of green H2 will decrease, and it will be slightly lower than gray hydrogen prices up to 2050. Blue H2 will also have its price reduced in the next 30 years, but the drop will not be as sharp as the green H2. In addition, by 2050, the H2 production will be more than five times the amount produced nowadays, and 15% of the production will be blue H2% and 85% will be green H2. Finally, the markets are betting on investments amounts around USD 15 trillion across the H2 chain over the next 30 years (see Figure 7).[17,183–186]

### Table 2. Hydrogen production processes comparison in terms of cost, efficiency, and cleanness.

| Process                  | Feedstock          | Energy     | Efficiency [\%] | Cost [US$ kg⁻¹ of H2] | Cleanness  | Ref.                  |
|--------------------------|--------------------|------------|-----------------|----------------------|------------|-----------------------|
| Steam reforming          | Methane            | Heat       | 70-85           | 1.03-2.08            | No clean with emission | [4,187–189] |
| Steam reforming with CCS | –                  | –          | –               | 1.22-2.9             | –          | [4,187–189]           |
| Partial oxidation        | Methane/heavier oils/coal | Heat       | 60-75           | 0.36-3.17            | No clean with emission | [4,29,190,191] |
| Auto-reforming           | Methane            | Heat       | 60-75           | 1.48-1.70            | No clean with emission | [4,29,190,191] |
| Gasification             | Dense liquid and solid fuels/coal | Heat       | 75-85           | 0.96-1.34            | No clean with emission | [4,187–189] |
| Gasification with CCS    | –                  | –          | –               | 1.2-2.2              | –          | [4,187–189]           |
| Electrolysis             | Water              | Electricity | 40-60          | 5.10-6.80            | Clean with no emission | [4,184,192,193] |
| Photocatalysis           | Water              | Solar      | 2-18            | 8.43-10.36           | Clean with no emission | [4,89,107,191] |
8. Conclusion

Hydrogen is a raw material essential for the petrochemical industry, for ammonia synthesis, and for a clean source of energy. However, the environmental benefits depend on the way of \( \text{H}_2 \) production. It is the same situation for electric cars, and if electric energy source comes from FFs, the environmental impact of electrification is drastically reduced.

As previously described, the current industrial processes to produce \( \text{H}_2 \) from FFs release into the atmosphere a huge amount of \( \text{CO}_2 \), eliminating any positive contribution to the environment. The understanding of these processes can inspire us to reach cleaner alternatives.

The challenge for the next 30 years is to replace FFs by a clean source of \( \text{H}_2 \), such as water. Nonetheless, although the process of producing \( \text{H}_2 \) from water is totally clean with no emission, being able to consider it as green hydrogen, the production from methane, for example, is approximately four times cheaper. Given this scenario, a tremendous effort must be done by governments, companies, and scientists if our society wishes to optimize \( \text{H}_2 \) production via WS technology, making it competitive with the current energetic matrix.

Water is essential to our life, and for this reason, alternative sources of water must be studied to avoid competition between drinking water and \( \text{H}_2 \). Thus, water unfit for human consumption, such as wastewater and seawater, can be interesting sources to produce clean energy with social responsibility. In addition, there are uncountable challenges that must be addressed to expand the source of water for WS. The major limitation found in WS processes is the overpotential and low kinetics of reactions in the cathodic processes and especially in anodic ones. Thus, low-cost, efficient, and stable catalysts must be researched. These catalysts should be composed of Earth-abundant elements and present high performance even operating under mild conditions.

Another aspect to be considered is the decentralization of the \( \text{H}_2 \) production processes. The concept of small plants can introduce the production of \( \text{H}_2 \) on-site and minimize the logistic costs and environmental impact. Furthermore, the use of 3D printing technology opens a plethora of possibilities.

Therefore, this review expounded the main challenges faced by the production of a cleaner and green \( \text{H}_2 \), and we believe that this can help to bring a reflection on the next steps toward a green hydrogen economy implementation based on \( \text{H}_2 \) production from water sources.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

electrolysis, green energy, hydrogen, hydrogen fuel, hydrogen production, water splitting
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