REVIEW PAPER

Sun, heat and electricity. A comprehensive study of non-pollutant alternatives to produce green hydrogen

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Summary
Water-based hydrogen production is currently an attractive research field, as it provides a greener method to produce hydrogen than existing alternatives. Green hydrogen is expected to progressively replace fossil fuels, which are highly harmful environmentally. This paper presents a critical analysis over time of the main water splitting technologies currently in use for sustainable hydrogen production. As a result of the critical analysis, all the studied techniques have been ordered chronologically in the way that it is possible to understand how new materials have driven to new techniques, more efficient and less expensive. This allows having a complete vision of these technologies. A high level of maturity has been reached in electrolysis, while other techniques still have a long way to go, although many improvements and relevant advancements have been made over the years. The paper offers a global and comparative vision of each technology. From this, it is possible to identify the different paths where efforts are needed to make water-based hydrogen production a mature, stable and efficient technology.

KEYWORDS
chronological review, electrolysis, green hydrogen production, photolysis, technical study, thermolysis, water splitting techniques

Abbreviations: AEM, Anion Exchange Membrane; CCM, Catalyst Coated Membrane; CNT, Carbon Nanotubes; FC, Fuel Cell; FCH JU, Fuel Cell and Hydrogen Joint Undertaking; GDL, Gas Diffusion Layer; GHG, Green Houses Gases; HER, Hydrogen Evolution Reaction; HyCon, Hydrogen Concentrator; LHD, Layered Double Hydroxide; LSF, Lanthanum Strontium Ferrite; LSGM, Strontium and Magnesium Co-Doped Lanthanum Gallate; LSM, Lanthanum Strontium Manganite; MEA, Membrane Electrode Assemblies; MFCI, Multilayer Flow Channel Inserts; MWNT, Multiwalled Carbon Nanotubes; NSTF, Nanostructured Thin Film Electrodes; OER, Oxygen Evolution Reaction; PBI, Polybenzimidazole; PE, Polymer Electrolyte; PEFC, Polymer Electrolyte Fuel Cell; PEM, Proton Exchange Membrane / Polymer Electrolyte Membrane; PFSA, Poly Perfluorosulfonic Acid; PS, Polystyrene; PSF, Polysulfone; PTFE, Polytetrafluoroethylene; RAFM, Reduced Activation Ferritic/Martensitic; SMR, Steam Methane Reforming; SOEC, Solid Oxide Electrolytic Cell; SOFC, Solid Oxide Fuel Cell; SPE, Solid Polymer Electrolyte; SPEEK, Sulfonated Polyetheretherketone; URFC, Unitized Regenerative Fuel Cell; WGS, Water-Gas Shift; YSZ, Yttria-Stabilized Zirconia.

1 | INTRODUCTION

Currently, several alternatives can be selected to produce hydrogen according to the raw material used in production.[1] From an annual global production of 70 Mt,[2] most hydrogen today is produced from fossil fuels and emits CO_2 (grey hydrogen)[3-5] while sustainable hydrogen production, generally from renewable energy, without pollutant (green hydrogen),[6,7] is still in the process of growth[8-10] Figure 1, shows that 76% of the current world's hydrogen production is derived from natural gas, via steam methane reforming (SMR), gaining much prominence in the last decade, as it corresponded to 48% in 2010.[11] Other processes for hydrogen production are from coal gasification (22%), and water electrolysis only contributes with 2%.[12,13]

Interest in hydrogen production methods arises in view of the fact that hydrogen plays a very important role in industrial processes.[14-19] Figure 2 shows that 42% of the pure hydrogen produced is used to manufacture ammonia (NH_3). This has been the main pure hydrogen demand for decades. However, from 2010 more than half demand is employed in hydrotreating processes in refineries. The remaining 6% is divided between other uses,
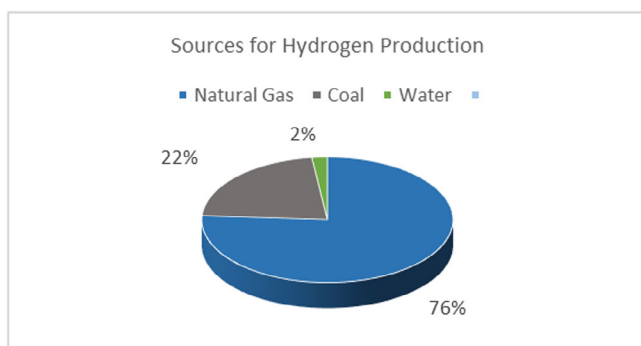

FIGURE 1 World's hydrogen production classified by raw material[12,13]
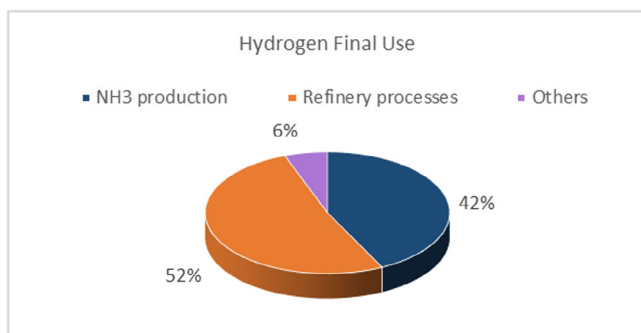

FIGURE 2 Hydrogen uses classification[12,13,20-24]

including methanol production, hydrogenation of fats, synfuel production and, of course, fuel cells feeding for both stationary and transport applications.[12,13,20-24]

The direct consequences of hydrogen production methods based on conventional fossil fuels are: greenhouse gases production,[25] inherent dependence of fossil fuels,[26] and the requirement of hydrogen purification stages to guarantee hydrogen purity degrees about 98% (depending on the hydrogen application).[27,28]

Based on the above, the hydrogen production from water is becoming increasingly important[29-31]; to the point that, following European directives and reports of the Clean Hydrogen Joint Undertaking, framed in EU Green Deal and Hydrogen Strategy,[32-34] research on the production of hydrogen from water becomes a priority, among other alternatives such as biomass, within the technologies proposed to make a transition to more sustainable energy systems.[35-39]

Then, according to Figure 3, the amount of energy required for the water splitting depends on the temperature in the sense that below 100°C (water in liquid state), the energy supply must be mostly in the form of electric power. Above this point, as the temperature increases, the water turns into steam and the contribution of energy in the form of heat counteracts the amount of electrical energy necessary for water splitting.[40] Therefore, for the hydrogen production from water, the required energy can be supplied in different ways like solar radiation, thermal energy or electric energy.

Consequently, water-based hydrogen production processes can be classified according to the nature of the energy being used, Figure 4: *photolysis*, when energy comes from solar radiation; *thermolysis*, when the source is the applied temperature; and *electrolysis*, when the division of water is done by electrical energy.

Several methods have been studied to generate hydrogen using water splitting techniques.[29] Although electrolysis has been used for industrial applications from the XIX century,[41,42] most water splitting techniques have been out of scientific and industrial priority attention until practically the beginning of the nineties of the last century. Consequently, many of these techniques still have little production efficiency, so there is much room for improvement.[43]

After carrying out a previous analysis of the main review articles, which are developed in the state of the art of hydrogen production techniques from water, Table 1 is presented, highlighting their contributions and motivating the completion of this review. Some are reviews of photolysis, including works focused on technology,[44-47] and those that also include the chronology of the advances.[48,49] The literature on relevant thermolysis reviews is limited as well, with some work

FIGURE 3 Energy demand for water splitting
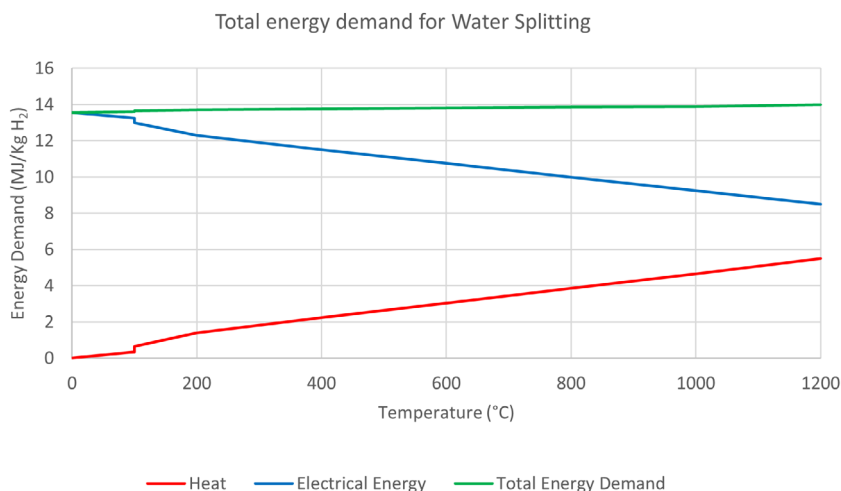
FIGURE 4 Sources for hydrogen production based on water splitting
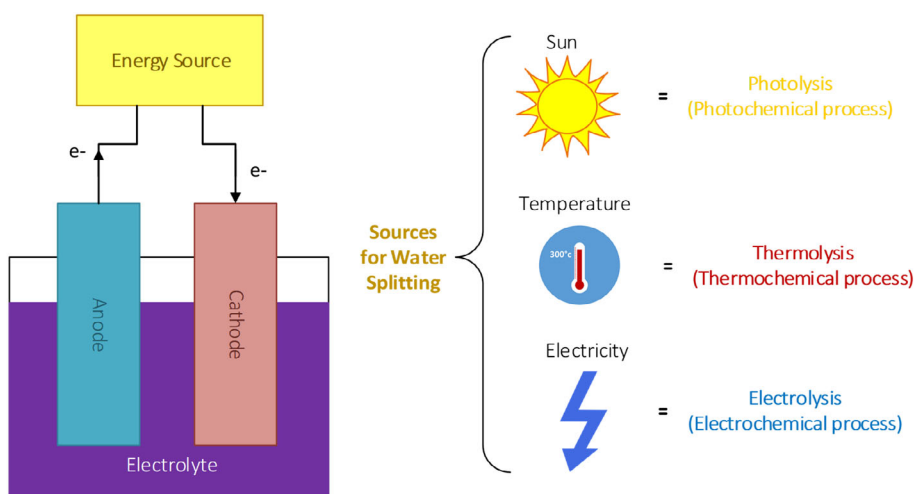
focused on the technical field.[50-52] The reviews regarding electrolysis are numerous, mainly technical,[53-62] but also historical.[29,63,64] As for works that consider various technologies, there is a relevant review on thermolysis and photolysis,[65] as well as few relevant reviews that also include electrolysis,[66,67] most of them from a broader view that includes polluting hydrogen production methods without analysing water splitting in such detail,[68-74] all of them focused on technical analysis.

The novelty of the authors' proposal is visualized through Table 1, since it carries out an important chronological analysis of all the main technologies, as well as updates previous works. This is of great relevance due to the strong impulse that is being given to research for the production of large quantities of green hydrogen.

Compared to previous publications, in main water splitting technologies currently in use for sustainable hydrogen production, no previous works have been found than include the analysis of the three renewable sources (sun, heat and electricity), from a chronological

and technical perspective, being the main novelty of this review. For this reason, this paper analyses the three main techniques for green hydrogen production, comparing their advantages and disadvantages from a qualitative and quantitative point of view. As a result, the studied techniques have been ordered over the time with the aim to understand how new techniques arise from the development of new materials and the commitment to overcome the drawbacks of the earlier techniques. In chronological order, the main drawbacks that each technology have presented, and the challenges overcome today will be revealed. This analysis, compared to the previous literature, provides a comprehensive view of the three main technologies, so that the advances, challenges, and how they have been reached can be visualized graphically and specifically. In this way, the main objective is to establish a source of extensive information, correspondingly classified and ordered in time, which serves as a basis for the improvements of the technologies analysed here. This entails taking not only the references

TABLE 1 Author's contributions regarding literature review

Ref.	Author	Sun[a]	Heat[b]	Electricity[c]	Chronology	Technical
44	Liu et al	✓	-	-	-	✓
45	Basheer et al	✓	-	-	-	✓
46	Giri et al	✓	-	-	-	✓
47	Al-Ahmed et al	✓	-	-	-	✓
48	Bak et al	✓	-	-	✓	✓
49	Maeda	✓	-	-	✓	✓
50	Mao et al	-	✓	-	-	✓
51	Mehrpooya et al	-	✓	-	-	✓
52	Safari et al	-	✓	-	-	✓
53	Shiva et al	-	-	✓	-	✓
54	Ursua et al	-	-	✓	-	✓
55	Wang et al	-	-	✓	-	✓
56	Chi et al	-	-	✓	-	✓
57	Babic et al	-	-	✓	-	✓
58	Hyung et al	-	-	✓	-	✓
59	Liu et al	-	-	✓	-	✓
60	Xiang et al	-	-	✓	-	✓
61	Cossar et al	-	-	✓	-	✓
62	Zhou et al	-	-	✓	-	✓
29	Carmo et al	-	-	✓	✓	✓
63	Paidar et al	-	-	✓	✓	✓
64	Zeng et al	-	-	✓	✓	✓
65	Pietro et al	✓	✓	-	-	✓
66	Idriss et al	✓	✓	✓	-	✓
67	Dutta et al	✓	✓	✓	-	✓
68	Singla et al	✓	✓	✓	-	✓
69	Epelle et al	✓	✓	✓	-	✓
70	Faye et al	✓	✓	✓	-	✓
71	Nnabuife at al	✓	✓	✓	-	✓
72	Hermesmann et al	✓	✓	✓	-	✓
73	Zhou et al	✓	✓	✓	-	✓
74	Younas et al	✓	✓	✓	-	✓
	Author's proposal	✓	✓	✓	✓	✓

[a]Photolysis.
[b]Thermolysis.
[c]Electrolysis.

of the same technology, but of the advances in all of them, which can well be extrapolated between them, as it has happened historically and is reflected in this review. The main scientific databases used in this review have been Wiley Online Library, Elsevier ScienceDirect and Scopus, Google Scholar and ResearchGate.

In Section 2, a chronological review of the main water splitting techniques for hydrogen production is made, starting with the techniques based on photolysis, continuing with the techniques that use the heat for decomposition and ending with the electrolysis processes. In Section 3, the different techniques studied are discussed and they are compared from the point of view of efficiency and the amount of hydrogen production. Finally, the conclusions are compiled in Section 4.

2 | SUN, HEAT AND ELECTRICITY FOR WATER SPLITTING-BASED HYDROGEN PRODUCTION. UNDERSTANDING THE TIMELINE

The first source used for water splitting was electricity; in 1789, Adriaan Paets van Troostwijk and Jan Rudolph Deiman published the results of their experiments on the decomposition of water by static electricity.[75] They used an electrostatic machine to generate electricity that was discharged by golden electrodes in a Leyden jar (a primitive capacitor manufactured using a glass jar with layers of metal foil on the outside and inside) filled with water. This experiment could be considered the first in demonstrating the water electrolysis process, however, traditionally the authorship of water electrolysis has been given to William Nicholson and Anthony Carlisle in 1800, but it seems that their only discovery was the used electricity source, the voltaic pile invented by Alessandro Volta that same year. The controversial fact of who first discovered water electrolysis has been discussed over years. Finally, the van Troostwijk and Deiman authorship has been agreed by de Levie[76] and Trasatti.[77] One century later, in 1888, the first industrial water electrolysis process was developed by Santos et al.[78] Since then and until now, new water splitting techniques have emerged to reach a solution for hydrogen production without harmful emissions, reduced energy consumption, cost, and maintenance and, all this, with high efficiency, durability and safety.

2.1 | The Sun: Inexhaustible resource

There is an important research line focused on trying to take advantage of the solar radiation to produce hydrogen.[79] Thermal and photonic processes are the most promising.[80] Thermal processes imply solar energy being converted to heat, which can either be used directly, stored or converted to another energy type. By contrast, in solar photonic processes, photons are absorbed directly by a photo-sensible material, without complete conversion to heat.[81] There are four basic subcategories: (1) sunlight is absorbed by isolated molecules in a solution (photocatalysis); (2) sunlight is absorbed by photoelectrochemical cells based on semiconductors, usually shaped like photovoltaic cell; (3) sunlight is absorbed by a biological system sensitive to light (photobiological system), usually algae and (4) a combination of all or some of the above processes.

Unfortunately, none of these processes/technologies currently have high efficiency, being around 18%.[82] It seems clear that these technologies
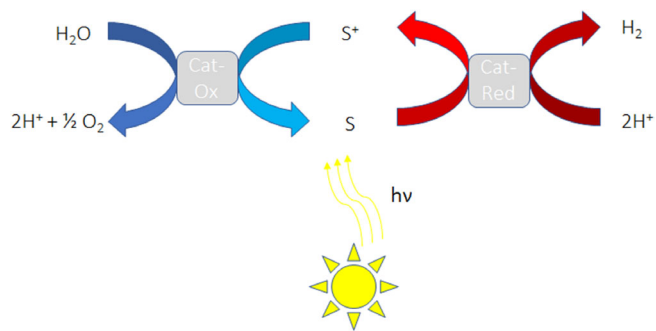

FIGURE 5 Scheme of photocatalytic system for hydrogen production

still have a long way to go to be competitive commercially speaking.

2.1.1 | Photocatalytic systems

From the point of view of hydrogen production, a photocatalyst system collects sunlight radiation to activate specific molecules that assist in the reactions for hydrogen production, Figure 5.

The first papers found in the scientific literature related to hydrogen production based on photocatalyst technique date from 1970s, when several works attempts to undertake direct photolysis for the hydrogen production as Bockris compile in Ref. 27 One decade later, Borgabello et al[83] demonstrate that depositing particles of CdS (Cadmium Sulphide) onto the catalyst, the hydrogen production is improved. In this sense, the search of new materials for softening water and for accelerating the redox reaction has predominated the working lines during the 90s and the beginning of the XXI century.[84-86]

Concerned by the efficiency of this technology, Bolton noted in[87] that almost all of the previous studies calculated efficiency using the half reactions separately rather than combining the two. There had only been one study of the entire process, which recorded a 7% efficiency. More recent works go over the improvement of existing methods,[88,89] with the aim to increase the process efficiency. In this sense, Li[30] proposes to use a technique called *junction*: construction of a hetero-junction at a photocatalyst interface, with the purpose of including a built-in electrical field that aides with charge separation and increases efficiency. Also, zeolite membranes were introduced for improved gas separation.

About the undesirable electron-hole recombination, what could also lead to low efficiency of photocatalysis, Ag/reduced graphene oxide/TiO_2 nanocomposites are proposed along with $LaTiO_2N$, Ta_3N_5 and $Sm_2Ti_2S_2O_5$ as relevant candidates for this issue during last decade.[90,91]

More recently, 2019, the Lawrence Berkeley National Lab has been working on a photocatalyst research. They claim to have found 12 new materials that will be useful for the photoanode of an electrolytic cell.[92] Different metal oxides were used during the experiments. They explored 174 different compounds, and the result was that structures composed of vanadium, oxygen and a third element were the most useful because of their tuneable results. In addition, the use of co-catalysts, along with CdS, has been shown to achieve system efficiencies of up to 12.8%,[93] depending on the production under different wavelength irradiation.

In this context, precious metals such as Rh, Pd, Ru, Pt nanoparticles have been widely utilized as co-catalysts, with several tests developed to find the suitable co-catalyst to improve the charge carriers separation in semiconductors.[90,94,95] However, the semiconductor modified with noble metals is not viable due to limited availability. Recently, it has been reported that the photocatalytic performance of semiconductors (Ta_2O_5 and TiO_2) was prominently influenced by the non-noble metal NiO core-shell structured co-catalyst. The reason is that the NiO inhibition nature suppressed the undesired back reaction.[96] Then, Ravi et al developed a system with CuO-NiO hierarchical nanostructures as a co-catalyst deposited on TiO_2 nanospheres for enhanced photocatalytic hydrogen generation. The formation of ultrathin NiO shell over the CuO core was confirmed. A high rate of hydrogen production of 26.1 mmol. h^{-1} g^{-1} was showed, under direct sunlight.[97] Current studies highlight in-situ co-catalyst formation and novel phosphorylation of NiAl-layered double hydroxide nanosheets as co-catalyst.[98-102]

2.1.2 | Photoelectrochemical cells based on semiconductors

This type of cells is composed of a photoanode and a cathode (metal) both immersed in an electrolyte and connected to an external circuit,[103] Figure 6.

The ideal materials for the electrodes are the ones that have a band gap of 1 to 2 V, because the ideal working voltage of the electrolysis cell is 1.229 V. Standard semiconductors such as gallium arsenide and indium phosphate have been shown to have high efficiencies in the case of hydrogen production.[104]

The first well-known semiconductor-based cell for the photolysis (dissociation of molecules by the effect of light) of water was studied in 1972 by Fujishima and Honda.[105] In their experiment, TiO_2 was used in the anode and platinum in the cathode. The cell was chemically biased due to the different pH levels in each side of the system.
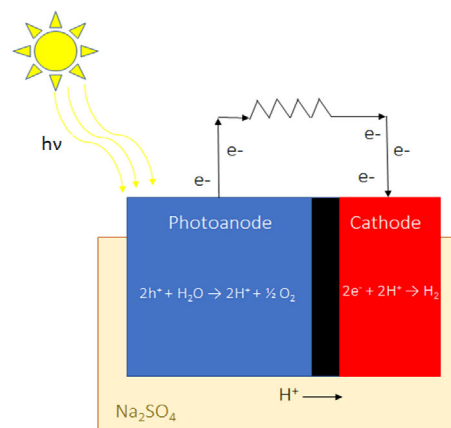

FIGURE 6 Scheme of photolytic cell based on semiconductor technology

In a study published in 1983, Murphy et al[106] tested a semiconductor comprised of two *p-n* couples made of gallium arsenide as a hydrogen generator using water photolysis. Up to that time, photoelectrochemical devices had efficiency rates around 1%, while the two cells junction reached 8% conversion efficiency of sunlight to hydrogen. Apart from these devices, it is possible to find photo-aided electrolysis cells with efficiency of 10%, higher than previous cases, but with the drawback of the cost of electrical power required.

With experimental results, authors concluded that low efficiency values, even in the two-cells junction device, were due to both corrosion of the materials from exposure to the highly alkaline electrolyte and because of the recombination of hydrogen and oxygen, due to difficulties of separating the two gases in an effective way. Then, photolysis cells were not yet suitable for hydrogen mass production.

With the aim to identify the factors which have effect on the photolytic cell, during the 80s Bockris et al attempt to model the hydrogen evolution reaction derived from the photo-induced current.[107] They conclude that hydrogen production rate due to photocurrent not only depends on semiconductor physical properties (doping density, for example) but it also depends on the surrounding electrolyte solution and the sunlight wavelength.

During the last decade of the 20th century, the interest of researching in this technology decreases and hardly one half hundred published works have been found. These works can be grouped in two: (1) those where authors propose a photocatalytic cell implementation, the effect of the etching treatments, the metal loading and the mixing of two semiconductors,[108,109]; and (2) those that focus on the use of alternative liquid electrolytes like HCl,[110] or H_2S.[111,112]

Fortunately, the interest in photoelectrochemical systems reawakens in the last years as it can be seen in.[30] Then, contemporary authors recover research both in new materials for photoanode[113] ($BiVO_4$ had a theoretical efficiency of 9% and Ta_3N_5 returned 15% theoretical efficiency), and new nanostructures to build the photoelectrochemical cell[114] (a vertical nanorod based on Ta_3N_5 to form the photoelectrode). However, this material is highly unstable and completely degrades in a few minutes. To this problem, some solutions can be found in[115] and,[116] where the hole storage layer based on ferrihydrite in the first case, and $Ni(OH)_x/MoO_3$ in the second, prolongs the lifespan of the photoelectrochemical cell for 6 and 24 h respectively.

Not only photoanode in photoelectrochemical cells have captured research attention but also photocathode development. Then, in an attempt to approximate to theoretical photocurrent density value (14.5 $mAcm^{-2}$, this is due to the incompatible light absorption of planar structures, and it equates to 18% efficiency), Paracchino et al[117] and Luo et al[118] have recently proposed a novel nanowired structure. On this, cuprous oxide (new material) is growth over a layer of titanium oxide (old material, remember original Fujishima and Honda design).[105] In each case, authors achieve, respectively, photocurrent values above 7 $mAcm^{-2}$ (7% efficiency) and 10 $mAcm^{-2}$ (12.82% efficiency). Currently stand out layered selenophosphites photocatalysts and improved Ag-sensitized TiO_2.[119-125] Photoelectrocatalysis report typical photoanodes of $BiVO_4$ and Ta_3N_5, with still low efficiency, and real pilot implementations with a short-term 100 kg/day H_2 production.[126-128]

2.1.3 | Photobiological cells

It seems that during history, practical application of photosynthetic processes for energy generation has not received enough attention. In this sense, it is relevant to remind that all fossil fuel reserves have their origin in photosynthesis, and additionally photosynthesis is responsible for all the energy stored in form of biomass.[129] Then, as could not be otherwise, it is possible to obtain hydrogen from a photosynthesis process.

Despite the belief that photobiological hydrogen production is relatively recent, hydrogen metabolism by photosynthetic organisms was originally reported in 1940 by Gaffron in.[130] It consists on employing microorganisms such as green algae and cyanobacteria, which in the presence of sunlight, are capable to generate hydrogen.[131]

Apart from green algae and cyanobacteria, there are other microorganisms like purple non-sulphur bacteria or dark fermentative bacteria which produces hydrogen.

However, the reaction depends on the physiological conditions of microorganisms, for example, the presence of some enzyme like hydrogenase or nitrogenase, some anaerobic conditions, etc.[132]

Despite the key role of the photosynthesis in the presence of fuels in the world, surprisingly, it is one of the processes that less attention has received along the history, and it has always been considered as a long-term challenge. After the theoretical formulation in 1940, experimental tests developed during the following decade demonstrate efficiencies near 10%, but with the drawback that algae saturates with the light intensity at solar irradiances above 0.03 suns (1 sun = 100 Wcm^{-2}) and photobiological hydrogen production ceases.[133] Thus, the main goal of the most published works found in the scientific literature has been to identify alternative species of algae that also support hydrogen photobiological production under a wider range of sun irradiance. This option has been chosen by several researchers during years,[134-136] and more recently, it has appeared the genetic engineering as solution to obtain mutant algae.[137] For example, Greenbaum et al[138] reduced the size of the antenna chlorophyll pool, allowing irradiances of higher value. This simply fact allows efficiencies of 15% to 20%.

In 2012, researches performed by the US Department of Energy in the Pacific Northwest Laboratory found a bacterium called cyanothece that is capable of producing both hydrogen and oxygen for 100 h uninterrupted,[139] supposing a great improvement to previous technologies. Recent studies distinguish Na_2SO_3 as oxygen scavenger, and enhanced production with Chlorella vulgaris and Chlamydomonas reinhardtii.[140-145]

Apart from new species or genetic engineering, other solution must be approached when the problem is the algae growth under nutrient deficiency. In this case, the photosynthesis activity decreases to help the algae to survival, and consequently the hydrogen production rate will also decline. Then, some authors begin to be concerned in this last decade about this issue (probably due to excess of contamination that sea water is suffering). In these cases, when the problem is not to find new algae species but looking for an alternative process that prolongs the life of the algae, the solution passes by introducing a new phase which consists on a dark anaerobic incubation before to the phase of light illumination for hydrogen production.[146] As a result, the hydrogen yield increases.

Some authors, dedicated to photobiological hydrogen production, guided their efforts toward new designs for photosynthetic systems. These new designs began to appear around the 90s, when photovoltaic, photocatalytic, photoelectrochemical and photobiological technologies had been established for several years. Wilner et al
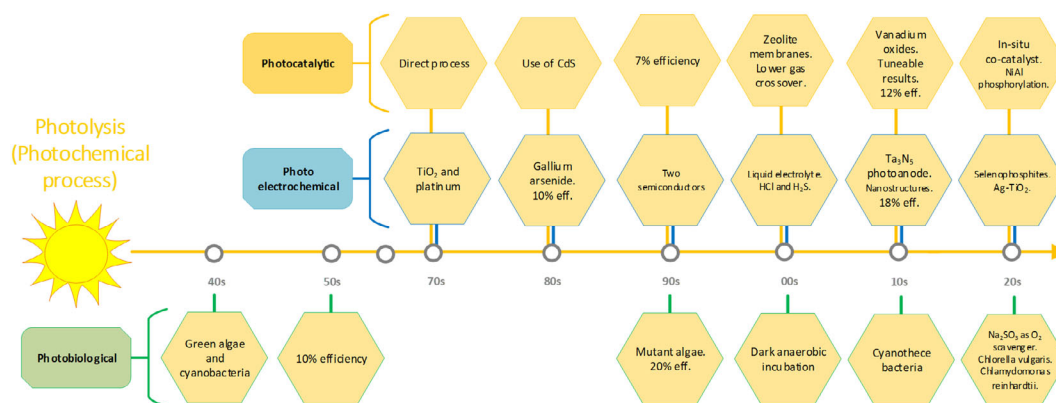
FIGURE 7   Main advances and historical achievements in photolysis technology

propose in[147] an hybrid system where the counterparts of the three different approaches (photocatalytic, photoelectrochemical and photobiological) come together in assemblies and have effect on water the photodecomposition. The hybrid system assures the organization of light-harvesting and subsequent hydrogen generation.

Another way to overtake the limitations that photobiological hydrogen production presents (saturation at high intensity light), passes by developing efficient photobioreactors. For example, a photobioreactor that is uniformly illuminated at the optimum light intensity solves the problems of photoinhibition and dark hydrogen uptake can be reduced. Additionally, a photobioreactor with high mass transfer capacity can remove easily the oxygen produced avoiding its further reaction with hydrogen.[148,149]

Finally, analysing all the cited works, all of them coincide that the maturation level of the sun-based hydrogen production technology will increase with the human concern about environmental problems; higher concern will equal be to a more mature technology.

The advances discussed in this section for each of the different techniques within the production of hydrogen using the sun are synthesized in the scheme of Figure 7, which represents the main advances and historical achievements in photolysis technology.

2.2 | Heat. A way to reduce the amount of required electricity

Thermal energy is an important resource when it comes to obtaining water splitting. Thermolysis is defined as the process at which water is heated to a high temperature until decomposed to hydrogen and oxygen. In practice, the temperature is required to reach 2500°C. That is why heat, as a source for water splitting, is more widespread as a resource to reduce the electricity needed in high-temperature electrolysis processes.

2.2.1 | Thermolysis

Direct thermal water splitting into hydrogen and oxygen is not achieved until the temperature is very high, generally over 2500°C.[150] For example, if it reaches 3000°C, a 64% dissociation can be obtained at 1 bar.

The interest in thermolysis cycles increased between the 70s and the 80s, during the oil crisis, and most of the cycles proposed took a nuclear energy source for heat, so operating temperature should remain below 900°C. Significant progress has recently been achieved regarding solar heat collectors and concentrators, on a megawatt scale. In this context, two-step solar heat cycles are characterized by operational simplicity, with large-scale production of H_2 from 1000°C.[151]

At recent years, Cu-Cl and Mg-Cl appear to be most promising low-temperature thermochemical cycles, without releasing any greenhouse gases (GHG) to the atmosphere while requiring a temperature higher than 550°C.[152] Some drawbacks of this technology are the toxicity of the chemicals involved during the cycles and their availability and cost. Another main drawback of this process, to avoid an explosive mix, comes from the requirement for an effective separation of H_2 and O_2. Although some thermolysis cycles produce both H_2 and O_2 in separate stages, they contribute partially avoiding their recombination and bypassing the need for costly gas separators.[151] To avoid this recombination, semi-permeable membranes based on ZrO_2, along other high-temperature materials, can be used at a temperature up to 2500°C.[153] This recombination can also be avoided when the product gas is rapidly cooled (within just few milliseconds) through a sharp temperature decrease of 1500°C to 2000°C. In that case, palladium membranes can be integrated.[154,155]

Nowadays, Cu-Cl has been identified as the most prospective cycles, with lower cost and highest efficiency,

while new developed Zn–S–I cycle shows best exergy efficiency.[51,156-160]

2.2.2 | Medium and high temperature electrolysis

Electrolysis processes above 100°C are considered as high temperature electrolysis, and when the process reaches 2500°C, it becomes spontaneous, as thermolysis. In general, the electrolysis thermal processes are divided into medium temperature (100°C to 300°C) and high temperature (600°C to 1000°C).[63] This type of hydrogen production from water splitting is most useful when there is already a heat source nearby, such as the heat expelled from a nuclear power plant.[161] One of the challenges in the electrochemical cells' design for medium-high temperature electrolysis is the lack of liquid electrolyte.[162] It was 1937 when this kind of cells, called zero gap cells, was applied for the first time to high temperature electrolysis cells - tests were run at 900°C.[63] However, curiously after this first approach to thermal electrolysis, zero-gap cells have become more popular in polymer electrolyte membrane (PEM) cells for electrolysis and their reverse, PE fuel cells, and recently even for alkaline cells[163] (alkaline and PEM electrolytic cells will be described in Sections 2.3.1 and 2.3.2 respectively).

After this early achievement, it was necessary to wait until the late 70s to find works focused on studying the hydrogen production from direct water splitting at high temperature.[164,165] In these works, both Nakamura[164] and Ihara[165] agree in their theoretical formulation for the process of hydrogen production using solar heat. Contemporaneously, other authors direct their efforts in defining aspects related to the solar absorbers like the cavity design[166] and the coating system[167] to increase its solar absorption capability.

Regarding the scientific literature, it could be said that the 80s would become the decade where the water splitting techniques based on temperature spread out toward both medium and high temperature. The first one, water electrolysis at medium temperature attempts to merge the advantages of materials stability employed in the cell from conventional water electrolysis with quick kinetic reaction from high temperature. As it is known, cell voltage descends with temperature, but it does not depend on operating pressure. However, combining temperature and pressure, water can remain in liquid phase up to 235°C at a pressure of 30 bar.[63] This was the aim of Abe et al,[168] when in 1983 contributed to the Sunshine Project helping to resolve Japan's energy shortage problems. The authors proposed a high-pressure, high-temperature new design for electrolytic cells. The cells were made from porous polytetrafluoroethylene (PTFE) impregnated with potassium titanate and they could operate above 120°C and 20 bar with an efficiency of around 90%. After this, other authors focused their works on increasing the operating temperature but analysing previously the possibilities that each cell technology offers.[169] Then, PEM technology for medium-temperature electrolysis was discarded up to the 90s because of its cost. Other researches focused on the modification of alkaline cells; for example, Divisek et al put in work cells based on NaOH/LiOH molten mixtures at 350°C, with hydrogen yield of 100% and 0.5 Acm^{-2}.[170] Finally, it was also possible to operate with solid electrolyte cells giving rise to the so-called high-temperature electrolysis.

Doenitz et al[171] studied the effects of high temperature on the production of hydrogen from a water source in 1980. Their goal was to improve upon the contemporary efficiency of electrolyzers in 1980—which were 75% with respect to the electrical energy input, using high-temperature methods. Their group found out that for the anode of these high-temperature electrolytic cells, it was necessary to use certain classes of materials to prevent undesirable side reactions or impurities in the hydrogen gas being produced. Their study was carried out with tubular structure cells operating at 400°C to 1000°C, and the traditional liquid electrolyte was replaced by yttria-stabilized zirconia (YSZ), Figure 8. This material was chosen for its desirable qualities such as cost and temperature-related stability.

Doenitz et al developed this work in 1975 in collaboration with the German Bundesministerium fiir Forschung und Technologie in the German HOT ELLY project, and this tubular design was used 10 years later by Siemens to define the structure of its Solid Oxide Fuel Cells (SOFCs).[172] The overall efficiency came upon 40% to 50% considering co-generation; the heat produced by the product gases was reused to warm the chamber and this made the system to operate at its optimum temperature.
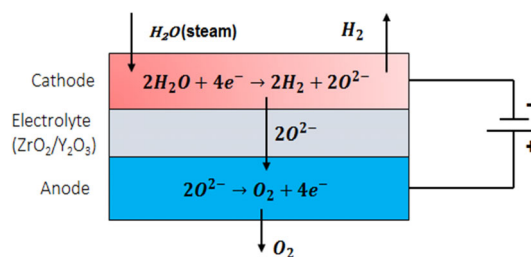

FIGURE 8 Scheme of a solid oxide electrolytic cell

In the main reviews of the hydrogen production technologies of the 1980s,[173] high-temperature vapour electrolysis stands out as a technique to be further developed in the next decade. Data of very high efficiency, compared to alkaline electrolysis, are collected, although it still cannot for reliability as high-temperature vapour electrolysis has only been tested in the laboratory. In the documented tests, for the temperature of 1000°C, a current density of 5 kAm^{-2} is obtained, for a voltage of around 1.2 V, and up to 7 kAm^{-2}, for a voltage of 1.4 V. The goodness, from the efficiency point of view, of high-temperature water splitting can be compared with alkaline electrolysis, where, to obtain similar current densities, a voltage between 1.9 V and 2.3 V is required.

In 1991, the Research Institute for Scientific Measurements of Japan carried out studies on the production of hydrogen from high-temperature steam electrolysis, using solar energy as a heat source for the process, with temperatures of up to 1000°C.[174] Given the high temperatures, a solid electrolyte is used, manufactured in ZrO_2 +- 8 mol% Y_2O_3 ceramic, for its stability with high temperatures and its high ionic conductivity. It was connected to the electrodes coated with porous platinum. During the thermal electrolysis process, the water vapour is delivered using Argon as a gas vector. The study concludes that high-temperature electrolysis obtains an efficiency of 98%, electrochemical efficiency of 71% and overall efficiency of 20% to 28%, which is high in comparison to the efficiency of the photovoltaic electrolysis of those years, 10% to 15%.[175] High efficiency is achieved from an affordable source of heat, and the development of finer electrolytic cells is proposed as a challenge, together with more efficient porous electrodes.

In subsequent studies, the question of the improvement of the solid membrane for electrolysis is addressed. In 1995, Naito showed experimental results of a system that makes use of a $ZrO_2–TiO_2–Y_2O_3$ (Ti-YSZ) membrane.[176] Using high temperature, vaporized water was dissociated while oxygen permeated through the membrane, by the difference in partial pressure of oxygen. The electrical properties of the system (Ti-YSZ) exhibit high electronic conductivity at high temperatures under low oxygen partial pressures.[177] Using the Ti-YSZ membrane higher hydrogen production was achieved, compared to the amount obtained with the YSZ membrane. This result indicates that as Ti-YSZ has higher electronic conductivity, then it is better as a membrane. The system is simplified, as there's no requirement of electrodes or electric power.

In the late 90s, studies for high-temperature water splitting continue with ferrites membranes.[178] Taumaura et al applied a mixed powder of $MnFe_2O_4$ with different mole ratios of CaO (or Na_2CO_3) to ferrite at 1000°C. This was considered as further progress in direct solar energy conversion to hydrogen production, as the required temperature was lower than the typical two-step water splitting by that time (1200°C to 2000°C).

Technology reviews of the 90s consider thermolysis as one of the three main electrolysis techniques, with a mature level. Main research focus was electrochemical stability of the electrode material, that could give a better context to make the technology commercially competitive, with the use of metal silicides.[179]

In the late 90s, in terms of improving this technology, Gomez et al[180] classified the areas of interest in Solid Oxide Electrolytic Cells (SOECs) for hydrogen production based on water splitting in three groups. (1) Current density, because at that time cells suffered delamination above 1 A/cm^2; (2) stack design and material type; and finally (3) manufacturing process, to make the whole process more economically feasible.

In the 2000s, Colomban et al test perovskite ceramic membranes for hydrogen production, with studies to determinate their physical and chemical behaviour, as a needed step to create successful commercial applications for the industry.[181] This gives conclusions about the importance to difference protonic species adsorbed on a membrane surface and the bulk protons.

Industrial solutions are presented in[182] for high temperature electrolysis (800°C to 1000°C), with Y_2O_3 +- ZrO_2 electrolyte, decrease in the electrical energy of up to 40% and production flow rate of 2.5 to 3.5 kWh/Nm^3H_2. The expected cost varied around 800 and 1000 €/kW, with efficiencies up to 80%.

About SOEC components,[183] the studies show Yttria-stabilized zirconia (YSZ) as the best option for the high temperature electrolyte, thanks to high conductivity, low cost and chemical compatibility with other component materials. Meanwhile, for intermediate temperature, high ionic conductivity makes strontium and magnesium co-doped lanthanum gallate LaGaO3 (LSGM) as suitable for the electrolyte, although nickel (Ni) is avoided due to reaction with LSGM. For both cathode and anode, Ni-YSZ and LSM-YSZ are the most used materials, with some recent studies indicating that lanthanum strontium ferrite (LSF) would be a better option than lanthanum strontium manganite (LSM). The SOECs planar form is preferred because of manufacturability and performance factor, although tubular form presents mechanical strength.

Considering that manufacturing costs of SOEC technology-based cells for hydrogen production are impractical for commercial interests, last decade is characterized by studies focused on improving the efficiency of SOEC technology-based hydrogen production technology. Petipas et al[184] discuss in 2014 the benefits of using an outside heat source to provide much of the energy needed for the solid oxide cells for water splitting to move
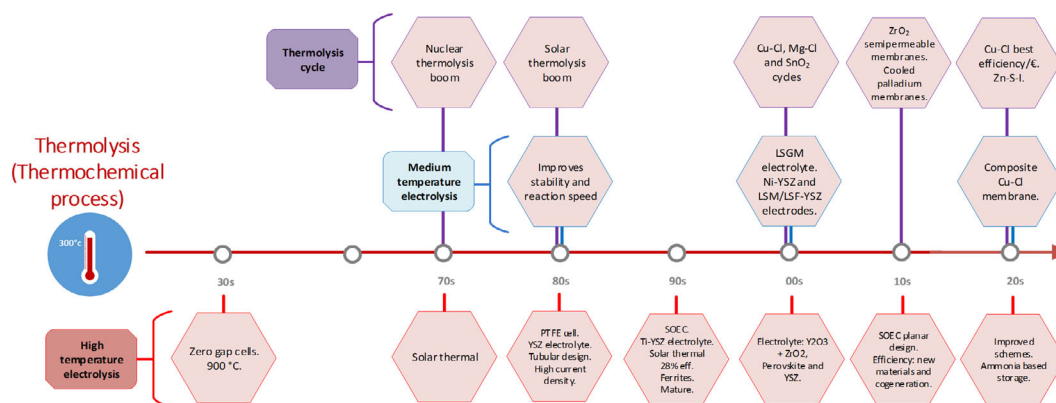
FIGURE 9 Main advances and historical achievements in thermolysis technology

forward. The study was based on heating the water into steam and then fed it into the SOEC electrolyzers. Once the 75% reaction is achieved, the hydrogen/water mix is fed out the electrolyzers to be cooled down to 25°C, which then removes the rest of the unreacted water in liquid phase, leaving behind the pure hydrogen. Next, the hydrogen is compressed to 3 MPa and cooled to return to room temperature. The achieved efficiency was 89% and authors suggest the possibility to improve it near 100%, if the waste heat produced by cooling the hydrogen is reused in the next cycle (to heat the water into steam). Late 2000s reviews consider the system efficient as the main influence on the hydrogen production cost,[182] estimating that the cost could be reduced from 50 \$/GJ in 2010 to below 20 \$/GJ in 2030,[185] to make it more considerable for commercial purposes. Additional researches are being focused on materials and form for SOEC technology,[183] microstructural modification,[186] degradation and performance,[187] and new materials doping.[188]

Recently, composite Cu-Cl medium-temperature electrolysis membranes[189,190] and the use of ammonia based thermochemical energy storage and layered-perovskite oxides electrodes for high temperature electrolysis stand out.[191-193] Heat and gas route improved schemes show energy demand reduction, especially in SOEC.[194]

The advances discussed for medium and high temperature water splitting are synthesized in the scheme of the main advances and historical achievements in thermolysis technology, Figure 9.

2.3 | Electricity. The most used source to obtain the highest hydrogen production rates from water

Electrolysis is defined as the chemical decomposition of water produced by passing an electric current through a liquid or solution containing ions.[195] The history of water electrolysis started in 1789, with van Troostwijk and Deiman research on the decomposition of water by static electricity, followed in 1800 with Nicholson and Carlisle using the voltaic pile to decompose water into hydrogen and oxygen.[196] Depending on the electrolyte nature, it is possible to talk about alkaline electrolysis or PEM (polymer electrolyte membrane) electrolysis.

2.3.1 | Alkaline electrolysis

An electrolytic cell has both electrodes, anode and cathode, submerged in a liquid alkaline electrolyte, Figure 10.[197-200] Despite the fact that the discovery of electrolytic water splitting occurred in acidic water, the alkaline environment is preferred in industrial plants, since corrosion is more easily controlled and construction materials are cheaper than the ones used in in acidic electrolysis.[196]

Regarding the history, in 1902, more than 400 industrial water electrolyzers were in operation, and in 1939, the first large water electrolysis plant with a capacity of 10 000 Nm³ H₂/h went into operation, meanwhile in 1948, the first pressurized industrial electrolyzer, by Zdansky-Lonza, was built.[196]

Based on experimental results, scientists soon were aware of the common problems that alkaline electrolysis presents: bubble effect, material stability and current density levels. Then, in 1976, Graziotti analysed how the power level supplied to the cell had a clear influence on the gas bubble effect: higher power, more hydrogen bubbles on the cathode, and consequently the cell efficiency decreases.[201] As it can be deduced, this is an unsolved problem that challenge to solve in.[64] Two years later, Lecoz and Gras showed that using chrysolite as a diaphragm could be stable against corrosion up to 180°C using particular concentrations of soluble potassium silicate. Then, at the next World Hydrogen Energy
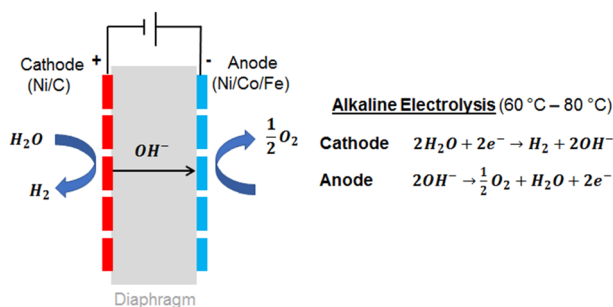
FIGURE 10 Scheme of an alkaline electrochemical cell

conference, Bailleux et al presented in 1980, that there was an insignificant amount of change in the physical properties of the diaphragm materials when run for 6400 h at 120°C, which shows that at that time the material was a desirable one.[201]

In the 70s, nickel along with stainless steel and iridium received attention for the first time to be used in the cathode.[202] Appleby et al experimented an electrolyte cell with a Teflon-bonded electrode as the anode, the separator was asbestos (after that, asbestos was dismissed merely for not being particularly efficient besides its carcinogen nature) and a solution of 24% to 34% of KOH. For the cathode, authors tested different materials like nickel, stainless steel and iridium alloy. Obtained results shown that iridium performed the best in alkaline solutions (current densities around 400 mA/cm^2, doubling the values achieved up to then), but this material would not be cost-effective. By contrast, stainless steel despite it was a cheap material, its inability to resist corrosion in a highly alkaline environment immediately eliminates it from the list of possible solutions. This has involved that nickel is being the most commercially extended material in cathode for decades.[203] In a review of 2010, Zeng et al have pointed out that there have been many advances in terms of nickel based alloys for use as electrodes in order to reduce the amount of damage caused with each usage of the cell, and to therefore prolong the lifespan of the electrodes.[64]

Next decade of the 80s, researches were driven towards the search of separator materials.[204] Potassium titanate and polyantimonic acid were shown as high-performance separators, from inorganic material, for alkaline electrolysis, while oxide-coated metallic is well considered, for long-term use. Between organic materials, polysulfone and polyphenylene sulphide were promising technologies, reaching stability temperature up to 120°C to 200°C, with needed improvements in surface properties, to solve their poor wettability. Vandenborre et al showed $NiCo_2O_4$ and $NiCo_2S_4$ as the best anode and cathode electrocatalysts.[205]

In 1983, Noranda Research Centre[206] shows that Teflon with potassium titanate has the lowest resistance factor as separator, although the fragility and hydrophobicity must be solved. Additionally, stability and good electrocatalytic performance are shown with nickel electrodes, plasma-sprayed with nickel/aluminium or nickel/stainless steel powders, and the most promising anode type tested to date was plasma-sprayed Ni/SS alloy.

Researchers from the late 80s show industrial achievements in cells with ceramic diaphragms and galvanically-deposited Raney nickel electrodes, with operating temperature of 100°C to 120°C, pressure between 1 and 5 bar, and energy consumption of 3.8 kWh/m^{3}H$_2$,[207] at 0.4 A/cm^2 and 100°C.

Research during the 90s also checked important electrodes improvements, at an affordable cost, using an electrocatalytic surface layer. Also, the increase of surface with Teflon-bonded diaphragms and Ni-layer alloys for electrodes. This improvement represents an energy input decrease of 0.96 kWh/m^{3}H$_2$.[208]

In the mid 90's, there were studies about anodic and cathodic behaviours of aluminium, iron, mercury steel (HgSt), chrome-nickel steel (CrNiSt) and platinum.[209] In 1996, Hu et al developed a multilayer structure cathode.[210] Meanwhile, Zirfon is also tested as a porous composite separator material composed of a polysulfone matrix and ZrO_2.[211]

New electrocatalysts are tested in the beginning of the 2000s, such as $MmNi_{3.6}Co_{0.75}Mn_{0.42}A1_{0.27}$ alloy, $LaNi_{4.9}Si_{0.1}$ alloy and Ti_2Ni alloy, and nickel-molybdenum coatings. The results demonstrated that the increase in molybdenum content causes activity for hydrogen evolution to increase as well.[212]

Electro-oxidation of ammonia on platinum (Pt) electrode was studied by Zhou et al,[213] showing that the cell efficiency can be up to 45%, while ammonia electrolysis with Pt electrode. Electrolytic cell efficiency could slightly be increased with higher KOH and ammonia concentrations.

In the late 2000s, the long-term stability of NiCoZn coating for hydrogen evolution reaction (HER) was investigated. It was found that the NiCoZn coating had a compact and porous structure.[214] Alternative studies tested the properties of multiwalled carbon nanotubes (MWNT) in anodes, obtaining enhanced exchange current density when compared to graphite anodes. The hydrogen production rate almost doubled that the rate obtained with traditional graphitic carbon electrodes, while the same overpotential was applied. This is caused by the interaction of OH^- ions with defects on the nanotubes. Therefore, the activation energy of dissociation of OH^- to O_2 is lowered, which significantly increases energy efficiency.[215]

In the recent years, 2015-nowadays, researchers try to fit together the different millstones that have been separately achieved along the previous decades. Then, regarding membrane in the cell structure, poly perfluorosulfonic acid (PFSA) material was evaluated as one of a few polymer membrane types that combine excellent alkaline resistance with extreme hydrophilicity.[216] Other studies also consider titanium (IV) oxide composite membrane to limit the usage of an asbestos separator, as it is hazardous for health among its low efficiency against the materials studies in the last two decades. This achieves 50% higher current density and hydrogen purity against asbestos.[217] The uses of carbon nano-structure composites for electrodes has been studied, obtaining the highest hydrogen production rate of 487 L/h-m^2 H$_2$ with the composite GC 73, composed by 70 wt% graphene and 30 wt% carbon nanotubes (CNT).[218] About electrolytes, there have been new improvements with the use of alkaline zinc hydroxide solution, composed of sodium zincate and potassium zincate in NaOH and KOH solutions, respectively. Results show that the application of these solutions can improve the hydrogen evolution rate minimally by a factor of 2.74 (with the use of sodium zincate) and 1.47 (when potassium zincate is applied) in comparison to the typical alkaline stacks.

Apart from the joined advanced on membranes and electrodes, a combined-design cell was proposed by Marini et al[219] in 2012. It consisted on two cell designs: a zero-gap configuration and an anion exchange membrane (AEM), similar to PEM cells from the point of view of structural configuration. Additionally, the zero-gap cell is immersed into a confined electrolyte, while the AEM cell requires a liquid electrolyte flow,[220] Figure 11. The electrodes are made of Raney-Ni doped with Mo (cathode) and Fe (anode) filled between by a felt made of cellulose meant to prevent the formation of gas bubbles. The system is placed into a large, temperature-controlled KOH bath to ensure smooth functionality. The anode is filled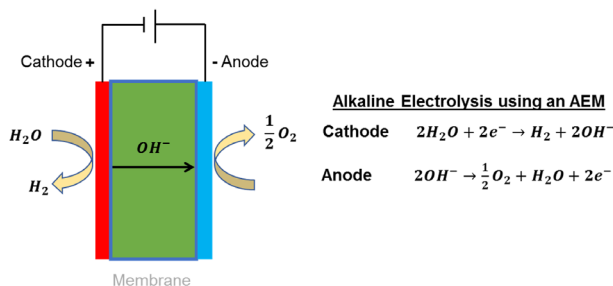 with KOH electrolyte solution, transporting the produced oxygen through electrolyte flow. The dry cathode produces hydrogen from water permeating the membrane from the anode.[221,222] Satisfactory results show current densities around 500 mA/cm^2 and efficiency above 60%. The first design mitigates the bubbles formed in the internal space of the cell while the second one reduces ohmic losses and make the system more stable. In this last case, authors propose to eliminate the bubbles in the AEM cell, in order to apply an overpressure on the electrolyte compartment; which will cause an effect similar to a "sneeze". These new proposals are being called *advanced alkaline electrolysis*. In this context, researches about AEM membranes using non-precious catalysts, different KOH electrolytes and operating temperature ranges are showing potential for AEM electrolysis in the next decade, 2020 onwards.[223-225]

Alternatively, there has been growing interest in Membraneless Electrolyzers (ME), where the use of a physical membrane as such is avoided. The process occurs in a chamber with an alkaline electrolyte and the reaction is carried out with porous electrodes as the fundamental axis, either with flow-by electrodes or flow-through electrodes, which are the two most relevant types of ME today. Recent reports prove better performance in flow-through electrode MEs.[226] Membranes are one of the challenges in electrolysis, due to their rapid degradation, which is why MEs are planned as a prominent alternative with low cost and enhanced lifespan. With first membraneless electrolysis cell patent in 2008, and scientific publications from 2015,[227] maximum efficiency of ME cells range between 64% and 82%, comparable to current alkaline electrolyzers. The main challenge of the technology focuses on the electrodes, and on finding a balance between their porosity and conductivity.[228,229]

Current novel alkaline approaches focus on composite membranes like polybenzimidazole incorporating graphitic carbon nitride nanosheets (PBI/g-C$_3$N$_4$) and pore-filling polytetrafluoroethylene/layered double hydroxide (PTFE/LHD),[230-234] and Ru nanoclusters on nitrogen-doped graphene as catalyst.[235] For AEM, Ni-based catalysts and polysulfone (PSF) or polystyrene (PS) hydrocarbon polymer backbone membranes they are the most accepted in more recent developments.[236-239]

FIGURE 11 Scheme of an anion exchange membrane (AEM) cell

Alkaline Electrolysis using an AEM

Cathode $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Anode $2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$

2.3.2 | Solid Polymer Electrolysis (SPE) or Proton Exchange Membrane (PEM) electrolysis

Solid Polymer Electrolysis (SPE) technology, also called Proton Exchange Membrane Electrolysis (PEM), works by a pair of electrodes (anode and cathode) being pressed against a solid polymer electrolyte (SPE), which is typically Nafion, Figure 12. Water and electricity are fed
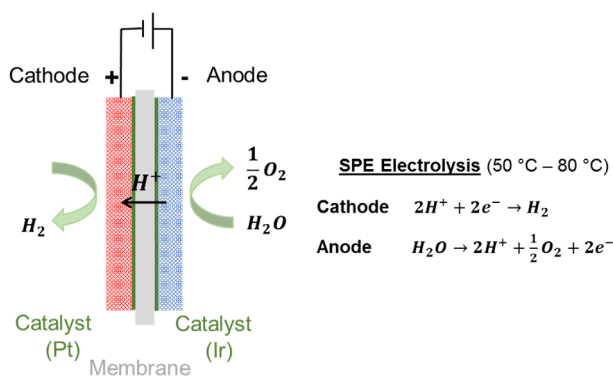
FIGURE 12 Scheme of a Solid Polymer Electrolyte (SPE) electrochemical cell

through the cell to produce hydrogen at the cathode, and oxygen at the anode. Usually, there are separators between the electrodes and the solid electrolyte, which are typically some kind of bipolar plate made of platinum (for cathode) and iridium (for anode) or a metal similarly resistant to corrosion.[240-243]

Similar to previous water splitting techniques, SPE technology began to receive attention in the middle of the last century, 1959, when Grubb presented its work where he developed an experimental study about ion-exchange membrane.[244] At that time, the only application found in this type of membranes was its use as membranes for the purification of salt water by electrodialysis. Fortunately, Grubb himself foreseen the potential of these membranes as *solid state battery electrolyte* (which then led to PE fuel cells).

After this, in 1966, Nuttall et al developed the concept of SPE electrolyzer for General Electric.[245,246] The proposal was presented as a way to replace the alkaline technology for large-scale hydrogen production.[247] The authors, aware of the system limitations at the time, predicted that this kind of system would achieve its best performance through the year 2000.

The positive aspects of PEM water electrolysis are[29]: higher current densities than alkaline electrolysis ($2 \, Acm^{-2}$ vs $500 \, mAcm^{-2}$), low gas crossover rate, allowing the SPE electrolyzer to work under a lower partial load range (0% to 10% vs 20% to 40% for alkaline electrolyzers), and compact design with solid structural properties that achieves high operational pressures. By contrast, the main drawbacks come from the SPE technology nature: special materials like noble catalysts to withstand adverse conditions (pH $\sim$ 2, cell voltage $\sim$2 V and current density $\sim$2 Acm^{-2}), and thicker although more resistant membranes to support high pressures. These two issues (catalyst and membrane) have led the way in PEM electrolysis research from the beginning of the 70s up to the present day. Additionally, other secondary aspects like current collector and

separator plates involved in the cell assembly have also received attention from researchers.

Already in the 70s, the General Electric Solid Polymer Water Electrolyzer,[248] that was operating at about 120°C to 150°C, seemed most promising in achieving the high energy efficiency and low capital cost goals, capable of operation at high current densities (over 1 Acm^{-2}) at a cell voltage of less than 1.8 V. As a consequence of the highly acidic environment, noble metals must be used as electrocatalysts. With funded programs, Nafion Du Pont developed 5 MW prototypes.[249]

In the 80s, as General Electric SPE system contuse its development and improvement,[250] new research in membranes and electrocatalysts are developed. New cation exchange membranes were developed, produced by radiation grafting of styrene groups on a polyethylene matrix, followed by chemical sulphonation of the resulting polymer. These membranes were supposed to have much less cost than the perfluorinated-hydrocarbon-based polymers which, so far, were the most used for SPE.[251]

Reviews form the 80s show that SPE issues include high cost of the Nafion membrane and poor stability of inexpensive anodic current collectors and catalysts in the acidic environment. An important phenomenon limiting achievable efficiency is back-diffusion of product hydrogen to the anode, where it is oxidized. This resulted in energy losses that were reported by General Electrics to be high as 10% at 150°C, and by Brown Boveri laboratories to be around 6% at 130°C.[252] This can explain why in that decade, alkaline electrolysis was still considered as the best option.

Next, in the 90s, new procedures for the preparation of SPE electrocatalyst composites were developed, where microparticles, based on noble metal electrocatalyst, were precipitated simultaneously inside and outside near both surfaces of a perfluorinated ion-exchange membrane, applying chemical reduction of cationic precursor salts. Nafion-based porous structures, with developments in Grenoble, can be coated on both faces of the membrane, and then catalysts is performed.[253] Nafion is the most used electrolyte of the decade, with some progress in develop alternative membranes, like the Dow Chemical membranes.[254]

Studies of the polymer electrolytes also tried to reach higher temperature materials, while maintaining hydrolytic stability. Liquid crystal polyesters, polybenzimidazoles and some polyimides show stability at 200°C. Polyphenylene sulphides, polysulfones, polyketones and some polyimides showed stability, in reasonable grade, at 300°C, while no polymer was found stable enough at 400°C.[255]

In the early 1990s, around 1993, SPE technology (introduced by General Electrics in the 70s), start to be

named as PEM (proton exchange membrane) by the science literature, and the meaning is extended as a system coating or pressing two electrodes onto a membrane used as electrolyte being recognize as the most promising candidate for low temperature production.[256] New research works go ahead with the improvement of the materials stability, as membrane water electrolyzers remain more expensive than alkaline, using IrO_2/Ti electrodes on both sides of Nafion membranes, what obtain much lower anodic over voltages and better stability, due to lower cathode sensitivity to poisoning, that Pt electrodes.[256]

In the late 90s, studies about materials continue to achieve higher temperature than the 125°C to 150°C range, with polymers as polyether ketones, polyether sulfones, polybenzimidazoles and polyphenyl quinoxalines. SPEEK (sulfonated polyetheretherketone), showing stable performance, up to 300°C is comparable to existing commercial ionomer membranes.[257] Great advanced in SPE electrolyzers can be found in this decade, especially focused on modelling and simulation.[258,259]

In the 2000s, more of these simulations allow to study electrolysis performance, showing that the high anode overpotential is the limiting factor.[260] Reviews show that a lot of R&D work was done in the field of PEM electrolyzers, but high price has limited their mass production, due to membrane, noble metals electrocatalyst (Ru, Ir, Pt), water systems and constructional material (Ti). A composition at 40% to 50% of RuO_2 is similar to activity of pure IrO_2, and parameters of electrolysis with $RuO_2(30\%)$-$IrO_2(32\%)$-$SnO_2(38\%)$ as anode electrocatalyst with platinum 0.8 mg/cm^2 are almost similar to electrolysis with iridium anode electrocatalyst with 2.0 to 2.4 mg/cm^2. Also, electrolysis at increased pressure of 30 bar, reached by PEM, shows an improvement of volt-ampere characteristic in comparison with electrolysis at atmospheric pressure.

Active surface area, electronic resistance, specific activity and structure are main parameters properties to be enhanced if high efficiency and performance of PEM want to be achieved. Development in new electrocatalysts showed the best result with an $Ir_{0.6}Ru_{0.4}O_2$ anode and 20 wt% Pt/C cathode, with 1.567 V of cell voltage at 1 Acm^{-2} and 80°C using Nafion as membrane. This provided cell efficiency of 94.4% and an energy consumption of 3.75 kWhNm^{-3} H_2 at 1 Acm^{-2}.[261] Also novel manufacturing process for catalyst-coated membrane (CCM) was developed to manufacture membrane electrode assemblies (MEA) for PEM, revealing that the sprayed Nafion layers are very effective for increasing the reaction interface between PEM and the electrode catalyst layer.[262,263]

At the end of the decade, scientific works are focused on polymeric membranes properties. Glassy polymers were generally used for manufacturing hydrogen-selective membranes. Size variations on these membranes adjust the discrimination ability. Main commercial polymers used for H_2-selective membranes are Ethyl cellulose or Polyetherimide. H_2-selective membranes are able to tolerate higher compression and temperature.[264]

In last decade, 2010–2020, with 50 bar studies, non-noble electrocatalysts cobalt-glyoximes. Although less efficient than platinum and also less sensitive to poisoning, they can replace it, reducing costs by almost a factor of two and paving the way for the large-scale development of PEM technology.[265]

Recent scientific works[53] show that the most commonly used membranes are perfluorosulfonic acid polymer membranes such as Nafion, Fumapem, Flemion and Aciplex. Nafion membranes (115, 117, and 212) have high current densities (2 A/cm^2), high proton conductivity, high durability and good mechanical stability. Pours titanium plates are being used as current collectors due to good electrical conductivity, mechanical stability, and corrosion resistant, with promising results. They act as current collectors and gas diffusion layer (GDL) for both sides of the MEA, enclosed by bipolar plates. Also, titanium grids/meshes/felts, carbon current collectors and stainless-steel grids are used, but the electro-chemical performance is lower. Separator plates are typically made of titanium, stainless steel and graphite but these materials are high cost, with some operational drawbacks, so many studies are focused on precious metal coatings and alloys to protect the titanium plates. Separator plates and current collectors are responsible for the 48% of overall cell cost. Noble metal-based electrocatalysts are used such as Pt/Pd-based catalysts as cathode towards the hydrogen evolution reaction (HER) and RuO_2/IrO_2 catalysts as anode for oxygen evolution reaction (OER). Then, PEM electrolysis considerable achievements have been made in commercial criteria, but overall water splitting-based hydrogen production is resulting in only 4% of global industrial hydrogen consumption, so for future research direction, it should be proceed to achieve a more cost-effective solution. That is why it is possible to find researches focused on catalyst separation, recovery and recycling,[266] studies to analyse the PEM degradations issues,[267] and also PEM cells that can operate at higher current density, with typical 1 to 3 A/cm^2, up to 10 A/cm^2.[268]

In these years, the new concept of Hydrogen Concentrator (HyCon) yields high efficiencies combining multi-junction solar cells with proton exchange (PE) membrane water electrolysis, using a titanium hybrid fibre sinter function both as a porous transport layer and flow field. The cell shows high performance with a voltage of 1.83 V at 1 A/cm^2 and the HyCon module is capable of achieving an efficiency of 19.5% from sunlight to hydrogen.[269]

One of the newest works is published by Kaya et al in 2017.[270] Authors develop a numerical model validated with experimental results where the effects on the cell performance are analysed of two types of catalysts for the anode (Pt and Pt-Ir). The results demonstrated that membrane thickness affects the performance of the cell, the thinner the better, and that the temperature increases the production of H_2 within the cell.

Currently, one of the largest parts of the total cost of a PEM electrolytic stack is the bipolar plates that must be placed between each cell to evenly distribute the charge throughout the entire stack. For now, they are often made of titanium, which is very expensive, in comparison to the manufacturing costs of other materials. The reason other metals are not used is the production of oxides that create ohmic resistance, which develop on the surface due to the highly corrosive and acidic environment of the typical PEM cell. Lædre et al tested in 2017 several materials in order to determine which functions the best to be used as bipolar plates in a PEM electrolytic cell.[271] Even three types of steel were tested for their functionality, but it must be noted that they did not display an increase in current density until 1.5 V and that could be caused either by corrosion or by the undesired oxygen evolution reaction.

Arrived at this point, it can be understood what happens inside a PEM electrolytic and how it is possible to improve its performance making some changes in catalyst, membrane, bipolar plates or operating conditions. However, what about external factors like power supply, what effects does the interrupted power supply have on the cell? As it was mentioned, in alkaline electrolytic cells, the lower partial load range must be higher than 20% to 40% (to beat the gas crossover rate in liquid electrolyte), but in PEM electrolytic cell, this drops to 0%. In this case, it would be interesting to know the changes brought about by fluctuation in the electrical supply to the cell. This issue has been studied between 2010 and 2014 by several authors who present systems that have in common a PEM electrolyzer supplied by a photovoltaic panels.[272,273] Nevertheless, these works disagree in the degradation factor. Rakousky et al were the first who identified an operating window for the PEM electrolytic cell with minimum degradation rate.[274] He analysed the volatile current density effect that mimics the behaviour of the solar cells, from which these electrolytic cells are expected to get their energy. The testing of the degradation lasted for about six weeks and was run between zero and 2 A/cm^2, to discover the causes of cell degradation. The metric used to mark cell degradation was the increase in cell voltage. As it was expected, the cell run under the constant current of 2 A/cm^2 was the one that experienced the most degradation (0.19 mVh^{-1}). The good thing about these tests was that, compared to the cell kept at constant high current density, the cells subjected to a dynamic current density profile experienced very little damage (0.06 mVh^{-1}).

Apart from these research works focused on improving the different parts that integrate the structure of a PEM electrolytic cell, recently there are arising other papers dedicated to exploring new perspectives for water electrolysis. Then, in 2016 Schalenbach et al developed an exhaustive comparative experimental study about efficiency in alkaline and PEM electrolysis. Authors conclude that modified alkaline cells, with thinner separator diaphragm and microporous electrodes enable better efficiency than those cells with acidic Nafion membranes.[275] These modified structure alkaline cells consist on the AEM cells.

In the same way and also in 2016, in an attempt to estimate the round-trip energy efficiency of a hydrogen redox battery, Lamy proposed two alternatives for a Unitized Regenerative Fuel Cell (URFC) for storage of intermittent energy.[276] The URFC consists of a (PEM electrolyzer + PE fuel cell), and a (SOEC electrolyzer + SOFC fuel cell). As it can be deduced, both systems have in common their high cost in comparison with alkaline technology. Against what might be expected, experimental results show better efficiency for PEM URFC (40% to 50%) than for SOC URFC (20% to 35%).

It is important to note that, as happened in the 90s, when the scientific community accepted the most widespread use of the PEM nomenclature (proton exchange membrane) to the detriment of the odder SPE terminology, introduced by General Electrics in the 1970s,[256] a new transition takes place in its terminology in the decade of 2010. It is verified in the scientific literature that the extended term PEM, still very widespread, now refers to polymer electrolyte membrane,[277-279] with some mixed nomenclature meaning referred as polymer exchange membrane,[280] instead of its previous typical use of proton exchange membrane, given that it is this characteristic that sets it apart from other hydrogen production technologies. In addition, the term membrane is also excluded from the nomenclature associated with the technology, being referenced only simply as PE (polymer electrolyte), with extended use of PEFC (polymer electrolyte fuel cell),[281-283] where it differs from the term PEM, which remains used in this case to speak only of the polymeric membrane electrolysis,[284] and not of the devices or technology, as it has been done until now.

These days, minimum membrane thickness and maximum operating temperature are investigated with great potential in hydrocarbon membranes. Iridium is mature and stable as a catalyst, with improvements demonstrated mainly in mixtures with ruthenium, as well as
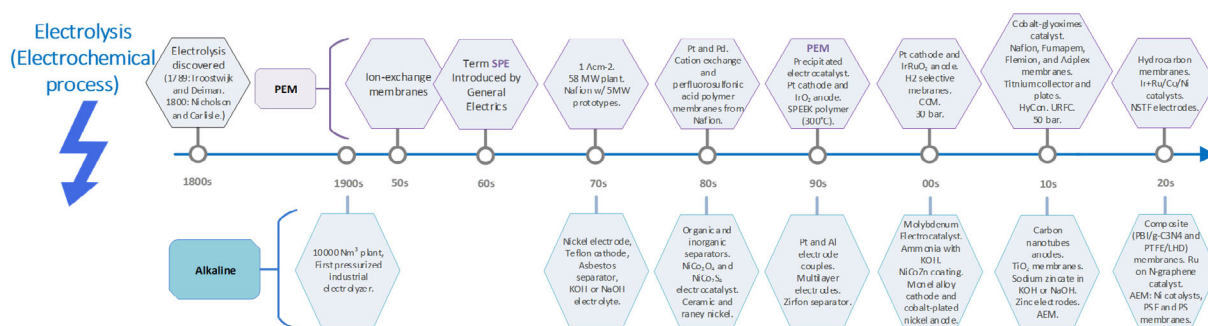
FIGURE 13 Main advances and historical achievements in electrolysis technology

TABLE 2 Technical characteristics of the water splitting-based hydrogen production alternatives

Water Splitting Technique		Ref.	Cell Prod. (Nm³/h)[a]	Cell Volt. (V)[b]	Cell Curr. (A/cm²)[c]	Cell Temp. (°C)[d]	Cell Pres. (bar)[e]	Cell eff. (%)[f]
Photolysis	Photocatalitic systems	93,291,292	-	-	-	-	-	0.5 to 12
	Photoelectro chemical semiconductor-based cells	104,293,294	-	1.2	14.5	-	-	2 to 18
	Photobiological	138,295,296	-	-	-	-	-	0.1 to 20
Thermolysis	Thermolysis cycle	152,297,298	<27	-	-	550 to 2500	-	17 to 55
	Medium temperature electrolysis	63,293,299	<10	0.95 to 1.29	0.3 to 1	100–300	<30	30 to 50
	High temperature electrolysis (SOEC)	293,299,300	<10	0.95 to 1.29	0.3 to 1	900 to 100	<30	40 to 70
Electrolysis	Alkaline cells	29,64,236,298	<1400	1.85	0.2 to 0.5	60 to 100	<30	59 to 82
	PEM cells	29,64,236,298	<400	2	1 to 2[g]/23	50 to 90	<35	65 to 84

[a]Cell Production rate.
[b]Cell Voltage.
[c]Cell Current Density.
[d]Cell Temperature.
[e]Cell Pressure.
[f]Cell Efficiency.
[g]Commercial units.

cobalt or nickel. Titanium suboxide and antimony oxide show promise. Nanostructured thin film electrodes (NSTF) stand out.[285-290]

The main advances throughout the history of alkaline electrolysis and PEM have been synthesized in the scheme of Figure 13.

3 | DISCUSSION

According to the chronological-technical review carried out about water splitting techniques, the main advances and milestones achieved in the different technologies throughout the different decades of scientific and technological development for hydrogen production are summarised in Table 2.

It should be clarified that these data refer to the most current references analysed in this review, in terms of more extended values and ranges. That is why, although there are case studies where higher values are obtained, as mentioned in the document, these cases constitute examples of an experimental prototype that are not consistent with the level of maturity and efficiency required by the different water splitting techniques nowadays. It should also be noted that not enough scientific literature has been found referring to some of the values of the specifications of water splitting technologies, such as temperature and pressure in photolysis, as well as the

values of photolysis production. That is why these specific references have not been considered sufficient to sentence a range of values faithful to technological reality in an extended way.

As shown, the efficiency in alkaline electrolysis and PEM is remarkable, as well as in the next level for the thermolysis technology, with better ranges for high temperature. Photolysis techniques are left behind in efficiency, given that despite not being a recent technology and having great advantages, as analysed in this review, its greatest advances have not been seen until recently and still has a long way for advancing in becoming a technology with greater technological maturity and with it its possibility of global commercialization. Cell production is also higher for electrolysis technologies, especially in alkaline cells, while thermolysis is way reduced and there's no relevant data for the lower cell production in photolysis technologies.

At this point, the different techniques and technologies of water splitting have been analysed from different perspectives, and once compared quantitatively, a synthesis of the main advantages and disadvantages thereof, Table 3, is then carried out. While all of them can be sustainable approaches to obtain hydrogen, photolysis highlights with a direct energy with zero cost. Thermolysis can be competitive with cogeneration systems, while

electrolysis depends on how the electricity is obtained, considering the efficiency and cost of the power sources, although there's already an electrical infrastructure that explain the commercial availability of the technology. Therefore, photolysis is an interesting alternative in what energy source refers, as costs is reduced. However, photolysis efficiency is not high enough yet, so several catalyst and biological components are in the trending view. While thermolysis can use the heat form different process in cogeneration, there are some specific issues with corrosion or toxic elements. Therefore, will not suit as a solution for every context, especially in small buildings lacking adequate space for a safe operation. The improvement of thermolysis is focused on different cycles proposals, new materials and the improvement of heat schemes. Electrolysis is already a commercial alternative to non-sustainable ways of hydrogen production. However, the cost of materials is still high, with still improvable lifespans. In addition, it depends on an external energy source, what adds the cost of acquiring and maintaining power electronics along with energy storage systems. Therefore, the green hydrogen obtained with electrolysis depends on a considerable investment. Regarding the social influence of the technologies analysed, it is necessary to consider, on the one hand, the operational impact, as well as the impact of the

TABLE 3 Qualitative comparison. Advantages and disadvantages of water splitting techniques

Water Splitting Techniques		Ref.	Advantages	Disadvantages
Photolysis	Photocatalitic systems	93,291,292	Energy zero cost. Emission-free. Readily available. Renewable source.	Long-term maturity. Low efficiency. Requires sunlight. Critical balance of the energetics of the solar conversion and solution-phase redox processes. Gas crossover.
	Photoelectro chemical semiconductor-based cells	293,294,301		
	Photobiological	138,295,296		
Thermolysis	Thermolysis cycle	152,297,298	Cogeneration systems. High efficiency. Sustainable. Maturity.	Expected development in the mid and long term (SOEC). Requires heat. Elements toxicity. Corrosion issues. High cost for small applications.
	Medium temperature electrolysis	63,293,299		
	High temperature electrolysis (SOEC)	293,299,300		
Electrolysis	Alkaline cells	29,236,295,301	Commercial maturity (alkaline). Easily sizeable. High efficiency. No pollution with renewable sources. Existing infrastructure. Electricity storage option. Maturity.	Power electronics development. Electricity source required. High cost compared to no sustainable processes as steam reforming.
	PEM cells	29,236,295,301		

production and disposal of the materials used, both in the hydrogen production system and in the necessary devices. In this sense, electrolysis from renewables does not produce pollutants and noise levels or temperature changes are minimal. However, the relative dependence of electrolysis on storage systems such as batteries must go hand in hand with alternatives in their production and recycling, as well as the use of microgrids with less dependence on these devices. Specifically in alkaline electrolysis, as well as in thermolysis, they are used that can create an impact on the health of users, with proper preventive maintenance being key, as well as a plant balance that integrates the appropriate control tools. These must include, referring to thermolysis, measures that minimize the heat impact of the installation. As for photolysis, and

especially photobiology, it makes use of natural resources that, with proper planning in production, can be easily obtained, and achieve synergy with algae harvesting companies used for hydrogen production.

In this context, an in-depth investigation into photolysis is necessary, given that it can be globally accessible and has great synergistic opportunities, while improvements in the energy dependence of thermolysis and electrolysis are proposed. Electrolysis plays a fundamental role, given its relevance and economic availability, in the rise and effective implementation of green hydrogen as a sustainable alternative in the energy sector.

Additionally, a more specific analysis of the promising materials and techniques is included in Table 4, for each of the specific technologies within the three main

TABLE 4 Recent promising materials and techniques of water splitting techniques

Water Splitting Techniques		Ref.	Promising materials and techniques
Photolysis	Photocatalitic systems	98	Phosphorylation of NiAl-layered double hydroxide nanosheets as co-catalyst.
		99-102	In-situ co-catalyst formation including: Cd and Ag2S decorated CdS; NiS on MnS/Mn0.3Cd0.7S; Platinum clusters; Core-shell Ag@AgSe with TiO_2.
	Photoelectro chemical semiconductor-based cells	122	Layered selenophosphites photocatalysts.
		119-121	Improved Ag-sensitized TiO_2.
	Photobiological	143,144	Na_2SO_3 as oxygen scavenger.
		142,145	Enhanced production with Chlorella vulgaris.
		140,141	Enhanced production with Chlamydomonas reinhardtii.
Thermolysis	Thermolysis cycle	156-158	Cu-Cl lower cost and highest efficiency cycle.
		159,160	Zn–S–I best exergy efficiency cycle.
	Medium temperature electrolysis	189,190	Composite Cu-Cl membranes.
	High temperature electrolysis (SOEC)	191,192	Ammonia-based thermochemical energy storage.
		193	Layered-perovskite oxides electrodes.
		194	Heat and gas route schemes.
Electrolysis	Alkaline cells	230-234	Composite membranes including PBI/g-C3N4 nanosheets and PTFE/LHD pore-filling.
		235	Ru nanoclusters on nitrogen-doped graphene as catalyst.
		236-239	Ni based catalysts and polysulfone (PSF) and polystyrene (PS) hydrocarbon polymer backbone membranes for AEM.
	PEM cells	288	Hydrocarbon membranes enhancing thickness and temperature.
		286,287,290	Iridium as a catalyst with ruthenium, cobalt or nickel.
		285	Nanostructured thin film electrodes (NSTF).
		289	Copper in the bipolar plates.

ones. In this way, it is possible to visualize which are the main approaches to take into account for the coming years, with the aim of giving a more effective improvement to the performance of these technologies for the production of sustainable hydrogen from water.

4 | CONCLUSIONS

This paper presents a detailed chronological and technical analysis, as well as an investigation of the existing solutions to produce hydrogen from water splitting. No scientific works have been found in the literature with this approach.

It provides insight into future goals for the differing technologies that exist today, as well as reviewing how far research has reached since the first discovery of electrolysis in 1789.

In the case of photolysis, energy comes from a totally renewable resource such as the sun, and organic techniques are used taking advantage of processes like photosynthesis in the plant world. Direct energy at zero cost is the great advantage of this technology, which still needs to improve its efficiency to be competitive, with the main research focusing on in-situ co-catalyst and different varieties of algae.

For the thermolysis, the necessary thermal contribution can come from natural phenomena, which makes it a renewable technology. It is also a very important alternative from the point of view of energy cogeneration, being able to take advantage of the heat generated, and in many cases not used, in large industries, thus helping to make better use of available energy resources. Therefore, its main challenges, throughout history and until now, focus not only on cell components such as the membrane and electrodes, but especially on thermal cycles, thermal storage and heat schemes.

In electrolysis, the supply of electricity can come from renewable energy sources, and this is the case in more and more practical cases, already commercially for years. With very high efficiencies, although energy dependent, the main research focuses on different types of membranes and catalysts, with alternatives to those of previous decades. Thus, the contribution of electricity from renewable energies such as solar energy or wind energy, not only makes electrolysis a way to obtain hydrogen as a zero-emission energy vector, but it is also key in remote or social emergency areas, where the electricity coming from the main electricity grid may be of low availability, quality or may have been interrupted by natural phenomena. This green hydrogen is already an important bet of many countries around the world and, probably, it will

be the most relevant means to combat the dreaded climate change.

From the study carried out, it can be inferred that in the near future, at an industrial level, green hydrogen will be produced by electrolyzers powered by renewable energies. In this regard, today, the most mature technology is alkaline, which means that although there is already a varied commercial offer of PEM electrolyzers, they still have great potential and development possibilities. Therefore, in the coming years, due to its compactness, cleanliness and efficiency, PEM electrolyzers are expected to dominate the portable and low-power market. However, waiting for them to drop in price, alkaline electrolyzers will dominate the high power market, especially from MW.

CONFLICT OF INTEREST
The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon request.

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