

# Advances in Alkaline water electrolyzers: A review

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## Abstract

The renewed concern for the care of the environment has led to lower emissions of greenhouse gases without sacrificing modern comforts. Widespread proposal focuses on energy produced from renewable sources and its subsequent storage and transportation based on hydrogen. Currently, this gas applies to the chemical industry and its production is based on fossil fuels. The introduction of this energy vector requires the development of environmental-friendly methods for obtaining it. In this paper, existing techniques are just presented and the main focus is made on electrolysis, a mature procedure. In turn, some developed proposals as previous steps to the hydrogen economy are presented. Finally, some lines of research to improve alkaline electrolysis technology are commented.

*Keywords:*

Hydrogen economy, hydrogen production, electrolysis

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## 1. Introduction

The world economy is constantly expanding. There are two influencing factors related to that expansion: the population growth and progress in personal comfort. Both factors affect the current fossil economy by increasing consumption and generating greater amount of greenhouse gases (GHG). The International Energy Agency (IEA) indicates a world consumption in 2015 of 9.383 Mtoe ( $1.1 \times 10^5$  TWh). This amount represents an increase of 18,23% and 99.64% over the past ten (2005) and forty (1975) years, respectively. Besides, CO<sub>2</sub> emissions in 2015 were 32.294 MTON, compared to 15.484 MTON in 1975 (109% increment) [1]. This situation is widely accepted as critical, hence worldwide environmental impact studies and environmental protection policies are generated. Moreover, the fact that fossil fuels are neither renewable nor evenly distributed across the globe leads to geopolitical conflicts and unequal situations.

Around the world, proposed solutions focus on the production of renewable energy. However, the share of renewable energies has not grown significantly (from 12.7% in 1975 to 13.5% in 2015). Besides costs issues, the global experience indicates that advances are needed to solve technical problems related to energy fluctuations produced in renewable sources. To achieve high integration of renewable energy, it is necessary to have the ability to accumulate the excess of energy to be consumed at a time when consumption exceeds production. Figure 1 shows the variety of available technologies for energy storage. While some technologies such as supercapacitors or flywheels are used to store a reduced amount of power (up to 10MW) for a short time (up to an hour) and redeliver it quickly, for the case raised, it is necessary to use other technologies such as Compressed Air Energy Storage (CAES), Pumped Hydro Energy Storage (PHES) or hydrogen.

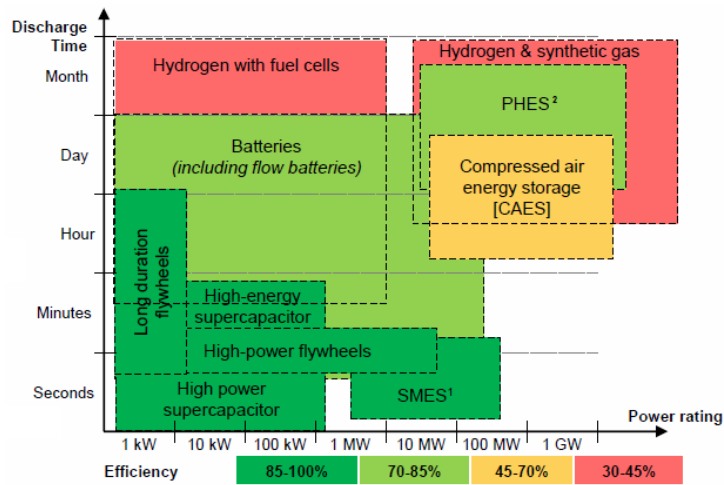


Figure 1: Current energy storage methods (taken from [2]). <sup>1</sup>SMES: Superconducting Magnetic Energy Storage, <sup>2</sup>PHES: Pumped Hydro Energy Storage

So far, the most common way to store large amounts of energy is PHES. The biggest disadvantage of this technology is related to its requirements on specific geographical features for installation and political conditions. It is here that among the methods of energy storage, hydrogen production currently takes relevance for its energy density, high energy capacity and transportability [2, 3].

Moreover, in the same direction, there is the concern about pollution in the transportation sector. Along with the development of electric vehicles, the hydrogen appears as an interesting energy vector. Both technologies, electric and H<sub>2</sub>-based vehicles, share the benefit of eliminating urban pollution and, depending on the original source, reducing or eliminating pollution in the whole process [4]. The union of these two sectors, electricity and transport, generates what is disclosed as *hydrogen economy*. The *hydrogen economy* is stated as an integral solution for the problem of producing, storing and supplying energy including all

final uses while succeeding in GHG mitigation.

The industrial use of hydrogen dates from almost a century ago with a wide consumption in the chemical and oil industries (89% of consumption share) [5]. However, progress must be achieved in various issues in order to accomplish competitiveness of these technologies and develop this economic concept. Issues such as the efficiency and cost of production, storage and transport, are concepts that several companies, research centers and governments are developing.

Several reviews can be found that present the different technologies related to the use of hydrogen. Abdalla et al [6] published a review of hydrogen technologies making a detailed explanation and comparison of current storage methods. Zhang et al [7] present a brief and well-organized compendium of production, storage and electricity generation technologies. Dutta [8] summarizes development models for the hydrogen economy in various countries along with an explanation of hydrogen production, storage and utilization. Mazloomi and Gomes [9] discuss the economic aspects of centralized and distributed production. In addition, they present the risks inherent in the production, storage and distribution stages, proposing possible risk-reduction techniques.

At the same time, there are studies such as [10] that detail the steps to be followed in order to reach a mature *hydrogen economy*. Among those steps there are the Power-to-Gas [11, 12], the use of fossil hydrogen to power vehicles [13, 14, 15, 16] and the integration of electrolyzers with renewable energies in microgrids [17, 18]. All these developments bring hydrogen technologies taking into account the necessary economic issues in order for it to be sustainable over time. To do this, it will be necessary that companies, governments and research centers cooperate together in this direction [13].

This paper provides an overview of the hydrogen production technologies, specifically emphasizing production from alkaline electrolysis. Mueller-Langer et al [19] in their techno-economic assessment assure that natural gas steam reforming, coal and biomass gasification and water electrolysis will play a significant role in the short and medium term. Besides, electrolysis occupies until today a dominant position as it is the only technology that can use directly the power surplus from renewable and fluctuating energies like wind mills or solar panels [7] so it has a concrete perspective on the use of this type of energy as the axis of the hydrogen economy. Among CO<sub>2</sub>-neutral H<sub>2</sub> production, electrolysis highlights because it produces high purity hydrogen and it has an infrastructure already developed being a well-established technology [20, 21]. In the same direction, alkaline electrolysis is a mature and reliable technology which stands out from other types of electrolysis based on cost and simplicity [22].

The remainder of this paper is organized as follows. In Section 2, hydrogen production technologies are compared according to efficiency, costs and environmental consequences. After that, in Section 3, water electrolysis, as the most certain solution for ecofriendly hydrogen production, is described. Then, in Section 4, necessary developments in alkaline electrolyzers in the short and long term are displayed. Finally, conclusions in Section 6 reinforce the necessity to advance research to achieve the reduction of pollution through the hydrogen economy.

Figure 2 shows the different methods of hydrogen production presented in Section 2. It highlights the approach outlined in this paper, explaining its organization.

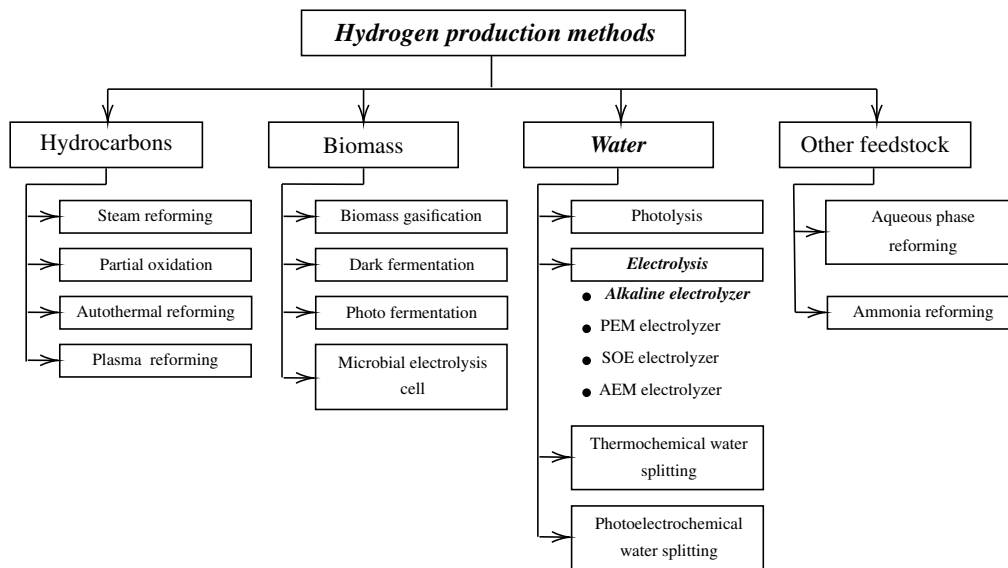


Figure 2: Taxonomy of hydrogen production with emphasis in this paper's objective (in boldface)

## 2. Hydrogen production methods

There are several methods of hydrogen production with different stages of development. Currently, its production is mainly based on the reforming of fossil fuels (78%) and coal gasification (18%). From the pending 4% of alternate resources, the main technology is the electrolysis of water as a byproduct from chlor-alkali process [23, 24]. Despite the current use of hydrogen produced by the last process, this technology will not be considered in the analysis because in the long term and taking into account the amount of hydrogen necessary, it would not be sustainable due to the chlorine produced at the same time.

In addition to the named technologies, in Table 1 it can be seen the selection offered by Holladay et al. [25] covering industrial methods and those which are being developed.

Some of the parameters used to compare different methods of hydrogen pro-

duction are efficiency, cost and environmental consequences. Efficiency, overall, compares the energy provided by the one obtained as the Lower Heating Value (LHV) of H<sub>2</sub> produced, whose ranges are listed in Table 1.

Moreover, the economic cost has the difficulty of analyzing mature technologies such as the steam methane reforming (SMR) with newly developed methods on a laboratory scale as photolysis. In turn, the technologies that rely on fossil fuels have different costs in case carbon capture and storage (CCS) approaches are considered or not. For instance, Parthasarathy and Narayanan [38] present SMR and coal gasification as the cheapest options (0.75 U\$Sk<sup>-1</sup> and 0.92 U\$Sk<sup>-1</sup> of H<sub>2</sub> produced, both without CO<sub>2</sub> capture) while electrolysis, considering the production of electricity with nuclear energy, costs between 2.56 U\$Sk<sup>-1</sup> and 2.97 U\$Sk<sup>-1</sup>.

Besides, Hosseini et al [39] present a cost comparison between some production methods as can be seen in Table 2. Production from fossil fuels was shown to be cheaper, even if CCS were required. Levene et al [40] consider that electricity costs have a great influence on the price of hydrogen produced by electrolysis, so it is concluded that the cost of electricity must be four times lower than the current price to have a competitive solution using solar and wind energy.

Concerning the environmental consequences, there are two commonly used rates. Bhandari et al indicate that most of the studies analyzed are concentrated in the Global Warming Potential (GWP) and some in the Acidification Potential (AP) [42]. These potentials measure the equivalent mass of CO<sub>2</sub> and SO<sub>2</sub> emitted per kilogram of H<sub>2</sub> generated, respectively. Figures 3 and 4 show the comparison of these rates for electrolysis from various renewable energy sources along with other methods of obtaining hydrogen. Marks above the bars in the graph high-

Table 1: Summary of methods for obtaining H<sub>2</sub> (adapted from [25])

Technology	Energy source	Feedstock	Efficiency	Maturity	Reference
Steam reforming	Thermal	Hydrocarbons	70-85% <sup>a</sup>	Commercial	[26]
Partial oxidation	Thermal	Hydrocarbons	60-75% <sup>a</sup>	Commercial	[26]
Autothermal reforming	Thermal	Hydrocarbons	60-75% <sup>a</sup>	Near term	[26]
Plasma reforming	Electric	Hydrocarbons	9-85% <sup>b</sup>	Long term	[27]
Aqueous phase reforming	Thermal	Carbohydrates	35-55% <sup>a</sup>	Mid term	[28]
Ammonia reforming	Thermal	Ammonia	NA <sup>c</sup>	Near term	-
Biomass gasification	Thermal	Biomass	35-50% <sup>a</sup>	Commercial	[29, 30, 31]
Photolysis	Solar	Water	0.5% <sup>d</sup>	Long term	[32]
Dark fermentation	Biochemical	Biomass	60-80% <sup>e</sup>	Long term	[29, 33]
Photo fermentation	Solar	Biomass	0.1% <sup>f</sup>	Long term	[29, 30]
Microbial electrolysis cell	Electric	Biomass	78% <sup>g</sup>	Long term	[34]
Alkaline electrolyzer	Electric	Water	50-60% <sup>h</sup>	Commercial	[30, 35]
PEM electrolyzer	Electric	Water	55-70% <sup>h</sup>	Commercial	[30, 35, 36]
Solid oxide electrolysis cell	Electric+Thermal	Water	40-60% <sup>i</sup>	Mid term	[31]
Thermochemical water splitting	Thermal	Water	NA <sup>c</sup>	Long term	-
Photoelectrochemical water splitting	Solar	Water	12.4% <sup>d</sup>	Long term	[35, 37]

<sup>a</sup>Thermal efficiency, based on the Higher Heating Values (HHV)

<sup>b</sup>Based on efficiency equation from [27]

<sup>c</sup>Not available

<sup>d</sup>Solar to hydrogen via water splitting and does not include hydrogen purification

<sup>e</sup>Percent of 4 mol H<sub>2</sub> per mole glucose theoretical maximum

<sup>f</sup>Solar to hydrogen via organic materials and does not include hydrogen purification

<sup>g</sup>Overall energy efficiency including the applied voltage and energy in the substrate. It does not include hydrogen purification

<sup>h</sup>Lower heating value of hydrogen produced divided by the electrical energy to the electrolysis cell

<sup>i</sup>High-temperature electrolysis efficiency is dependent on the temperature the electrolyzer operates at and the efficiency of the thermal energy source. If thermal energy input is ignored, efficiencies up to 90% have been reported [31].



Table 2: Cost of hydrogen production methods (from [39])

Process	Cost of H <sub>2</sub> (USDkg <sup>-1</sup> )
Natural gas reforming	1.03
Natural gas reforming + CCS	1.22
Natural gas reforming + PSA + CCS <sup>a</sup>	1.56
Coal gasification	0.96
Coal gasification + CCS	1.03
Wind electrolysis <sup>b</sup>	6.64
Biomass gasification	4.63
Biomass pyrolysis	3.80
Nuclear thermal splitting of water	1.63
Gasoline (for comparison purposes)	0.93

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<sup>a</sup>Current central H<sub>2</sub> production from Natural Gas with Pressure Swing Adsorption (PSA) used for H<sub>2</sub> purification up to 99.6% [41]

<sup>b</sup>Electrolysis using electricity generated by wind turbines

lights the different GWP values extracted by Bhandari et al from their sources [42]. It must be emphasized that these studies are based on Life Cycle Assessment (LCA), which comprises the construction, operation and end of cycle of each technology. It can be seen that electrolysis together with renewable sources produces less pollution than widely used technologies, even in cases of considering CCS. Although thermal decomposition has better results, it still needs to be developed. Besides, biomass gasification is slightly more polluting than electrolysis but it is a technology that also receives interest today.

Based on the previous study, Dincer and Acar [43] present an analysis comparing various technologies based on sustainability and costs. It is necessary to clarify that for the calculation of the environmental impact of electrolysis, these authors took the average value of all sources of electricity, including the grid. Therefore, due to the fact that the electricity network has higher polluting emissions, the GWP value of electrolysis appears as a non ecofriendly method. This is not the case when electrolysis is combined with renewable sources, as will be considered in this work.

While the electrolysis was the first commercial method of obtaining hydrogen [42], other methods such as SMR have taken its place and are today the processes used at industrial level because of their better efficiency and costs. However, facing the new optical of environment care and GHG emissions mitigation, electrolysis takes back relevance and the research is aimed at improving those two aspects.

Moreover, there are various methods of producing hydrogen which are ecofriendly and competitive. Currently, there is a strong research on the use of biomass, which is accepted as the substitute for the use of fossil resources [39]. How-

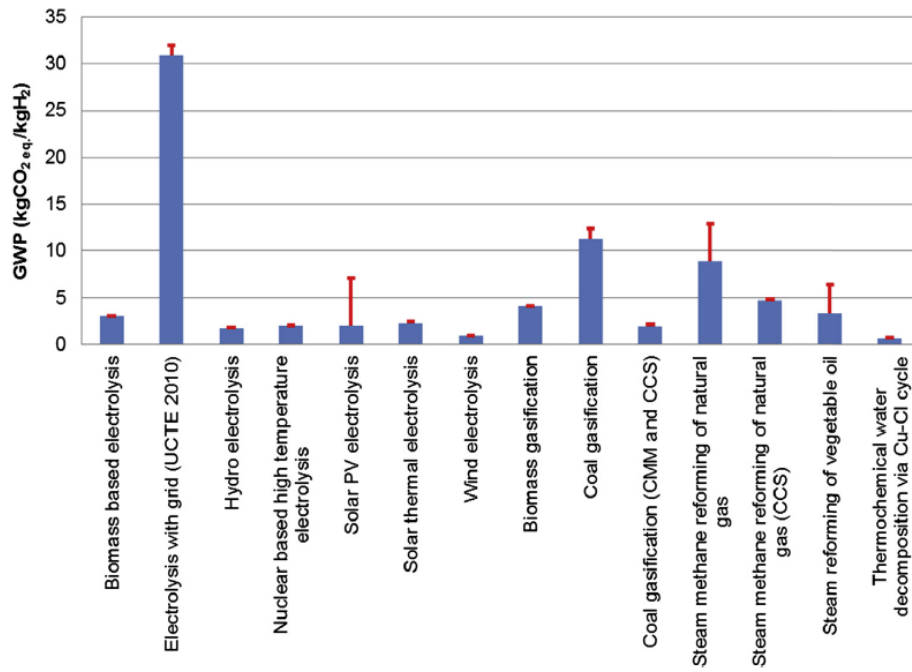


Figure 3: GWP for various H<sub>2</sub> production technologies (taken from [42])

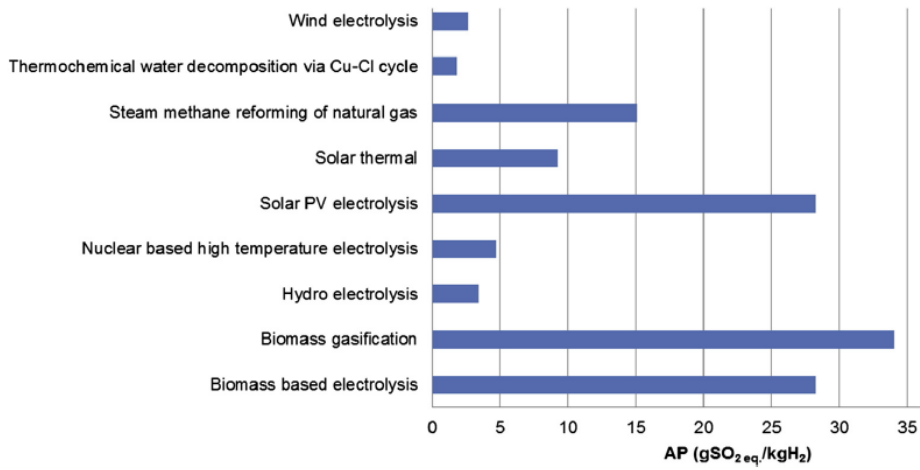


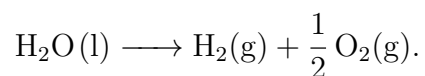
Figure 4: AP for various H<sub>2</sub> production technologies (taken from [42])

ever, these technologies require different levels of development and scalability testing, but promise to be competitive [20]. Among them, it is worth mentioning the case of microbial electrolysis, since it can achieve a high efficiency in the production of hydrogen and is considered versatile in terms of the various alternatives of application [44].

As stated in Section 1, electrolysis has the ability to take direct advantage of the surplus electricity from renewable energy sources that is a fundamental step in the development of the hydrogen economy. So from now on, this paper will focus on this technology.

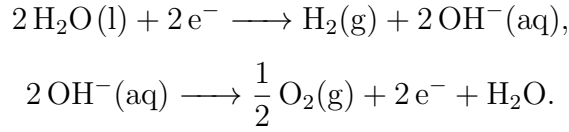
### **3. Water electrolysis**

Electrolysis is the method through which the water molecule is separated into hydrogen and oxygen by applying an electric current [42]. Although there are different methods, which are introduced below, they share the same global reaction



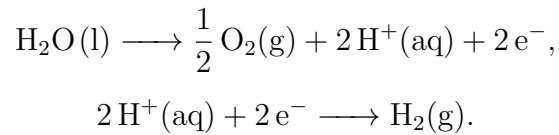
#### *3.1. Alkaline electrolysis*

Alkaline electrolysis highlights among other technologies since it is the one with greater maturity and the larger commercial outreach [43]. The system is constituted by a pair of electrodes immersed in an alkaline solution, usually potassium hydroxide (KOH) at a concentration of 25 to 30%, and separated by a diaphragm. At the cathode water is split to form  $\text{H}_2$  and releasing hydroxide anions which pass through the diaphragm and recombine at the anode to form  $\text{O}_2$  according to the following reactions:



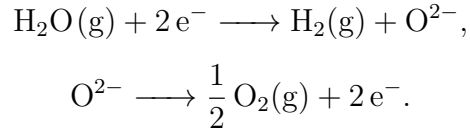
### 3.2. Proton Exchange Membrane electrolysis

The electrolyte in this case is a polymeric membrane with acidic nature that allows exchange of protons ( $\text{H}^+$ ), hence its name Proton Exchange Membrane (PEM). That membrane, along with the electrodes, form what is called Membrane Electrode Assembly (MEA). At the anode, water is oxidized to  $\text{O}_2$  and release protons that flow through the membrane and are reduced at the cathode to form  $\text{H}_2$  according to the following reactions [45]:



### 3.3. Solid Oxide Electrolysis (SOE)

Both Alkaline and PEM electrolyzers are known as Low Temperature Electrolyzers (LTE). On the other hand, a third option, Solid oxide Electrolyzer (SOE), is known as High Temperature Electrolyzer (HTE). Although LTE is a mature technology, HTE has the distinction of performing electrolysis of water vapor at high temperatures, resulting in higher efficiencies compared to previous options. Moreover, it has the possibility of using waste heat instead of part of the electricity needed [46, 47]. Despite this, they are not ready to be commercialized because they have durability problems due to the severe conditions. The reactions occurring at the cathode and anode are as follows:



### 3.4. Anion Exchange Membrane electrolysis (AEM)

A technology that is being developed is the cell with Anion Exchange Membrane (AEM). Schematically it has the same structure of a PEM cell with the difference that the membrane transports anions  $\text{OH}^-$  instead of protons  $\text{H}^+$ . In that sense, the reactions that occur in the electrodes are the same as for the traditional alkaline cells [48]. AEM technology brings certain advantages compared to the latter ones [49, 50]:

1. They do not present precipitation of carbonates due to the lack of metallic cations.
2. They show lower ohmic losses because the AEM is thinner than traditional membranes.
3. The membrane is less expensive than the PEM one.
4. It is not necessary to use a concentrated KOH solution, making installation less critic and easier to operate.

In addition, due to its basic condition, this type of electrolyzers does not require platinum-group-metal (PGM) catalysts such as PEM cells. Instead, there are experiences using transition-metal catalysts with suitable performances, which makes it cheaper [51, 52, 53, 54]. Moreover, a possible advantage over the traditional alkaline electrolyzers that is being studied is to be able to improve the purity of produced gases at high pressure [55].

A mathematical model was made by An et al [50] that was validated with experimental data found in the literature. In that work, the authors report that the performance of the cell improves at a higher exchange current density and liquid saturation and with a lower membrane thickness. However, a matter to be solved is the durability of the alkaline membrane since it has a low chemical stability [49, 56, 57, 58].

### 3.5. Comparison of electrolytic methods

The three main methods of electrolysis have various features and different stages of development, as can be seen in Table 3.

Because of its long tradition, alkaline electrolyzers are nowadays sold in greater numbers, although PEM models are competing with them. As can be seen in Table 3, the latter have important advantages over the former in relation to a higher current density, a greater operating range and a higher purity [45]. On the other hand, the biggest disadvantage of PEM electrolyzers lies in the durability of the components [62] and in the higher costs associated with titanium-based contact elements, such as bipolar plates and current collectors, and the high iridium charge of the electrocatalyst for Oxygen Evolution Reaction (OER) in MEA [63]. Because of this, the greatest efforts in the latter are devoted to the search for new materials. In spite of greater efficiency, SOE electrolyzers are still being developed for commercialization so this technology will not be deeply analyzed. Its efficiency close to 100% (in practice it can reach values of 90%) generates interest in the developments related to the improvement of durability and costs [64]. Despite these efforts, the SOE electrolyzers are far from reaching commercialization status [65].

In the research carried out by Felgenhauer and Hamacher [66] to BMW, different companies and models of alkaline and PEM electrolyzers are compared until

Table 3: Typical specifications of electrolyzers (taken from [43] and updated with information from [59])

Specification	Units	Alkaline	PEM	SOE
Technology maturity		Widespread commercialization	Commercialization	Research & Development
Cell temperature	°C	60-80	50-80	900-1000
Cell pressure	bar	<30	<30	<30
Current density	A cm <sup>-2</sup>	<0.45	1.0-2.0 <sup>a</sup>	0.3-1.0
Cell voltage	V	1.8-2.4	1.8-2.2	0.95-1.3
Voltage efficiency	%	62-82	67-82	81-86
Specific system energy consumption <sup>b</sup>	kWh Nm <sup>-3</sup>	4.2-4.8	4.4-5.0	2.5-3.5
Minimum partial load	%	10-40	0-10 <sup>c</sup>	-
Cell area	m <sup>2</sup>	3-3.6	<0.13	<0.06
Hydrogen production per stack <sup>d</sup>	Nm <sup>3</sup> h <sup>-1</sup>	<1400	<400	<10
Stack lifetime	kh	55-120	60-100	8-20 <sup>e</sup>
System lifetime	year	20-30	10-20	-
Hydrogen purity	%	>99.8	99.999	-
Cold start-up time	min	15	<15	>60
Investment costs	€kW <sup>-1</sup>	800-1500	1400-2100	>2000 <sup>e</sup>

<sup>a</sup>Typical commercial values, although laboratory experiments with a current density up to 20 A cm<sup>-2</sup> are reported [60].

<sup>b</sup>Excluding rectifier and utilities (0.4-0.8 kWh Nm<sup>-3</sup>)

<sup>c</sup>Vendors do not report a technical limit but it is known that there is gas contamination at high pressures and low current density that prevent reaching values close to 0 [61]

<sup>d</sup>According to a recent market survey

<sup>e</sup>High uncertainty due to pre-commercial status of SOE



the first half of 2014. In Table 4, it can be seen some technical data of electrolyzers from nine companies: CETH2/Areva H2Gen, Hydrotechnik, Hydrogenics, ITM Power, McPhy Energy, NEL, Next Hydrogen, PERIC and Siemens.

For large-scale systems, there are configurations commercially available formed by several stacks allowing greater production than the ones listed in Table 3. Another advantage of this type of configuration is the possibility to have a wider range of operation.

Although it is not explicit in the table, Felgenhauer and Hamacher say that efficiency is between 52% and 62% for alkaline electrolyzers and 57-64% for PEM systems, at the beginning of life (BOL) and 10 bar outlet pressure. Taking into account that the average of the efficiency degradation of the models analyzed by Felgenhauer and Hamacher is double for the PEM type (1.57%) than for the alkaline ones (0.78%), the former difference becomes less important, leading to an even situation throughout the life of the system.

In the study mentioned, an economic evaluation of these systems is performed and better outcomes for the case of higher alkali production are obtained. In Fig. 5 investment cost and the cost of annual operation and maintenance per produced power of hydrogen (LHV) are observed. Moreover, the best cases (AEL25+), that represent Alkaline Electrolyzers with a generation capacity over  $25 \text{ kg}_{\text{H}_2}\text{h}^{-1}$ , are shadowed.

Being the technologies in commercial state, Schalenbach et al [67] make a comparison between the alkaline electrolysis cells and the PEM cells together with a review of the challenges of both.

In Figure 6, it can be seen schemes of both cells with a similar configuration. The most important difference lies in the nature of the separator that divides the

Table 4: Technical data of commercial electrolyzers (taken from [66])

System	Generation capacity	Efficiency degradation	Maximum output pressure	Stack lifetime
	kgH <sub>2</sub> /hour	%/year	bar	hour
Alkalines				
A06	5.9	1.50	10	55000
A10	9.9	1.50	10	55000
A25	25.0	1.00	1	78840
A27A	27.0	0.50	13	87600
A27B	27.0	0.25	10	96000
A31	31.4	0.10	13	50000
A36	36.0	1.00	30	87600
A44	43.7	1.00	1	78840
A45	45.0	0.25	10	96000
A50	50.0	1.00	1	78840
A54	54.0	0.50	13	87600
PEM				
P09	9.0	1.17	30	70080
P11	12.0	2.50	14	100000
P21	21.2	0.50	35	80000
P22	21.6	2.50	14	100000
P47	47.0	1.17	30	70080

half-cells of H<sub>2</sub> and O<sub>2</sub> production: in the case of the alkaline electrolyzers, this is a porous diaphragm that allows the free circulation of the hydroxyls present in the alkaline solution, generally potassium hydroxide (KOH), which floods the cell [68], while in the PEM cells, it is a solid polymeric electrolyte (SPE) that provides the necessary protons for the process [45].

Behind the separator, there are electrodes whose surface is covered with elec-

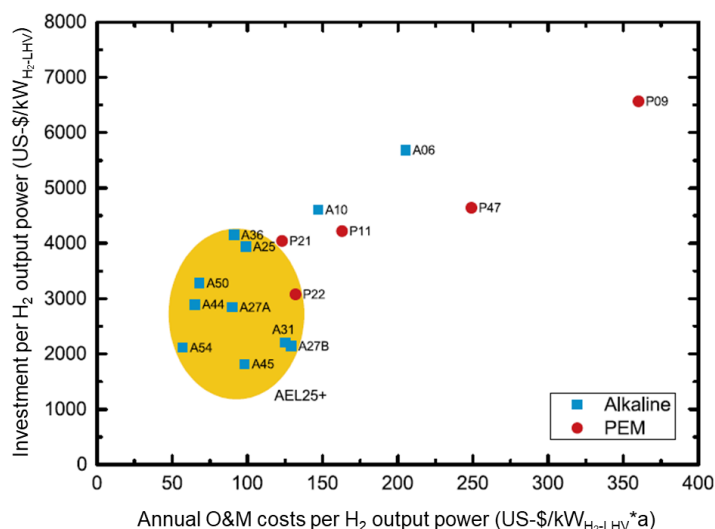


Figure 5: Investment cost and cost of operation and maintenance by produced power of H<sub>2</sub> (taken from [66]). The best cases (AEL25+), that represent Alkaline Electrolyzers with a generation capacity over 25 kg<sub>H<sub>2</sub></sub> h<sup>-1</sup>, are highlighted

trocatalysts that allow the reaction. These electrodes must be porous to allow the circulation of water, produced gases, electrons and ions [69]. In the case of the PEM cells and due to their acidity, only the platinum-group metals (PGM) have been tested commercially for being stable and having an acceptable ionic activity as electrocatalysts. However, the advances that have been made in the use of electrocatalysts with a transition metal base are promising. Such is the case of the transition metals of the first row (Mn, Fe, Co, Ni, Cu) as chalcogenides, phosphides, nitrides and carbides [70, 71]. In addition, the electrochemical properties of transition metal carbides (WC, Mo<sub>2</sub>C, TaC, NbC) have been tested for HER at medium temperatures (200-400 °C) obtaining a proper activity although a demonstration is still needed under realistic conditions [72].

That is why the electrodes are commercially made with an SPE base coated

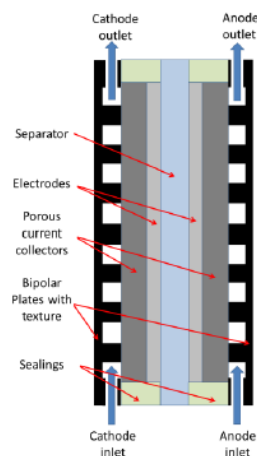


Figure 6: Schematic of an electrolytic cell (taken from [67]).

with platinum at the cathode and iridium at the anode. On the other hand, as the KOH solution provides the anions, the electrodes can be made as a metallic mesh, usually Ni. Moreover, stable catalysts made of Ni, Co and Fe are much more abundant and cheaper than their PGM pairs [67].

Since the Ni electrodes allow a proper electrical conduction and have sufficient mechanical resistance, it is not necessary to use collectors in the alkaline electrolyzers, therefore the electrodes are connected directly to the bipolar plate. On the contrary, the electrodes of the PEM cell require the support of the collectors to ensure the conductivity and structural stability.

The problems of durability [73] in the PEM cells lie in the replacement of protons by other cations losing conductivity [74], the loss of dimensional properties under temperature and pressure [75], the degradation by the formation of HF [76] and the ohmic losses by the oxidation of Ti present in the collectors and bipolar plates [77]. In contrast, alkaline electrolyzers are intrinsically more durable but it is important to be careful with the Ni dissolution when the cell potential falls below

1.23V, so it would be necessary to maintain a stand-by power that would hinder direct and isolated interconnection with renewable energies.

The study concludes that, for large-scale industrial water electrolysis, liquid alkaline electrolyzers seem to be more suitable because they are not limited to the use of precious and scarce metals. In turn, due to the different corrosion mechanisms in acidic and alkaline media, the latter show greater durability. Finally, the alkaline electrolyte is chemically stable and interchangeable, while the SPEs are vulnerable to the loss of conductivity due to impurities, chemical decomposition and thermomechanical deformation. As presented by the companies in Table 4, a tie situation can be observed in terms of the stack durability and a minor difference from the summary presented in Table 3. This is not in accordance with what was stated before but it could be justified by the efficiency degradation which was pointed out by Felgenhauer and Hamacher [66].

The main issues of each of the technologies that has to be worked out, are the outlined next. For the case of PEM cells:

- Designing of SPE membranes more durable thermomechanically and chemically.
- Finding other suitable catalysts than Ir.
- Counteracting the corrosion and low conductivity of passive layers that degrade anodic collector bipolar plates.
- Lowering diffusivity in the solid phase of membranes for greater purity.

In contrast, the challenges for alkaline cells, which will then be discussed in Section 4, are outlined as follows:

- Making porous electrodes that allow the effective evacuation of the bubbles and therefore decrease the ohmic fall.
- Optimizing porous alloys catalysts with Ni, Fe and Co.
- Preventing hydride formation and hydrogen embrittlement in Ni cathode.
- Reducing pores diameters of separators for greater purity.

#### **4. Developments in Alkaline electrolysis**

In recent decades, advances have been made in this type of electrolyzers called as advanced alkaline electrolyzers. The most important points of development are [21]:

- Zero-gap configuration. It consists of minimizing the distance between electrodes to reduce the ohmic losses.
- New materials for the diaphragm. Previously made of asbestos, the use of inorganic membranes is investigated. Some are based on antimony polyacid impregnated with polymers [78], on porous composite composed of a polysulfone matrix and  $ZrO_2$  (Zirfon) [79], or on polyphenil sulfide (Ryton) [80].
- Temperature increase. The temperature is increased to promote electrolytic conductivity and improve reaction kinetics at the electrodes.
- Electrocatalytic materials. Such materials are developed to reduce overpotentials at the electrodes.

A computational analysis of the citations made in recent years on electrolysis was developed by Ogawa et al [81]. The results indicate that the amount of publications related to this technology is increasing, and that the areas of microbial electrolysis and catalysts in alkaline and PEM electrolyzers are attracting greater interest. It is clear that although alkaline electrolysis technology is widely known, there is still interest in developing improvements in different fields, some of which are presented below.

#### *4.1. High temperature and pressure electrolysis*

The electrolyzers are currently designed for stationary operation. In turn, there are electrolyzers that produce gases at atmospheric pressure or up to 30 bar. So compression stages are required for storage at high-pressure levels. Against this, the opinions are divided between those who propose to design electrolyzers that produce directly the gases with greater pressure [82, 83] and those who assure that this is a loss of efficiency [84].

In the last group are Roy et al [84] who consider in their analysis the energy consumption in the auxiliary equipment and the loss of gas during the operation to conclude that atmospheric electrolyzers are more efficient compared to electrolyzers operating at pressures up to 700 bar. The percentage of increase in energy consumed reaches 16.66% at 700 bar, according to the calculations of the authors. At the same time, they consider that corrosion, hydrogen embrittlement, operation complexity, dynamic response and costs, make pressurized electrolyzers less favorable.

On the contrary, the first group claim that the energy needed to compress the gases grows more than the theoretical energy of dissociation of water. There are even projects that try to demonstrate with pilot plants the realizability of such a

Table 5: Development perspectives of selected parameters in alkaline electrolysis technology (taken from [83])

Specification	Symbol	Unit	State of the art	Short-term Development	Middle-term Development
Temperature	$\vartheta$	°C	70-80	80-90	>90
Pressure	$p$	bar	30	>60	>100
Current density	$i$	kA/m <sup>2</sup>	3-4	6-8	>10
Cell voltage	$U$	V	1.9-2.3	1.8-2.1	1.7-2.0
Voltage efficiency	$\Phi$	%	64-78	70-82	74-87
Spec. energy use, sys	$\Psi_{sys}$	kWh/Nm <sup>3</sup>	4.6-6.8	4.5-6.4	4.4-5.9
Part load capacity	$\theta$	%	25	<15	<10
Operating life	$\tau$	h	<90000	>100000	>120000
System durability	$\Pi$	y	<25	30	>30

solution, as the case of Brandenburg University of Technology Cottbus [83]. In the presentation of the project, they define the perspectives on the technology of alkaline electrolysis, as shown in Table 5.

Allebrod et al [85] assure to have succeeded in improving the efficiency of alkaline systems with an operating state of 240 °C and 37 bar. In turn, they propose a new design with electrolyte inside a porous structure allowing current densities up to 2 Acm<sup>-2</sup> and voltages not exceeding 1.75 V (typical value in commercial equipment). On the other hand, in the cost analysis competitive prices are obtained by not using precious metals.

Ganley [86] also experimented with electrolytic cells of high pressure and temperature (up to 87 bar and 400 °C). The results were promising given that the applied voltage is drastically reduced. However, the author raises objections about these results due to the possible mixture of products and corrosion of the electrodes that could have distorted the aforementioned values. Having said that,



it is necessary to design new experiments that allow to explain the observed phenomena.

In conclusion, it is theoretically possible to increase the efficiency of the system by increasing the pressure and temperature but there are still technical issues to be solved, among which cross-contamination of gases and materials stability stands out, respectively.

#### 4.2. Overpotentials reduction

The principle of alkaline electrolysis functioning has been widely described by several authors. In 2003, Ulleberg [87] proposed a model based on concepts of thermodynamics and heat transfer to obtain the package voltage, the produced gas flow rate and the thermal equilibrium of the system, as a function of the imposed current. These results were validated at the PHOEBUS plant in Jülich, where tests of photovoltaic cells, production and storage of hydrogen are carried out [88].

On the other hand, Ursúa and Sanchis [89] start from the same thermodynamic theory to define the ideal tension of water dissociation to construct an electrical model of the overpotentials. The final model has the same terms proposed by Ulleberg as can be seen in equation 1, where  $v_e$  is the voltage applied in the stack,  $N_s$  is the number of cells in a series configuration,  $v_{act}$  is the activation overpotential and  $v_{ohm}$  is the ohmic overpotential:

$$v_e = N_s(V_{rev} + v_{act} + v_{ohm}) \quad (1)$$

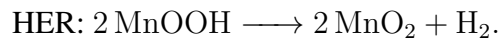
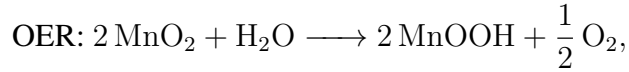
The first overpotential,  $v_{act}$ , is due to the polarization of the electrodes because of the approximation of the electrolyte ions to the surface of the electrodes, what is known as double layer effect. In her doctoral thesis, Roy [90] proposes the

calculation of the second overpotential,  $v_{ohm}$  from the conductivity of the materials in the path of the current and the presence of gas bubbles. This means that said overpotential includes both the electrical and the ionic conductivity in the electrolyte.

On one hand, Zouhri and Lee [91] propose a model to investigate the effects of properties of different materials on the ohmic overpotential, which influences the exergetic efficiency of alkaline electrolysis. In their work, it is shown that parameters such as membrane resistivity, distance between electrodes, bubbles, KOH concentration and temperature affect such overpotential. It is concluded that the greatest loss of efficiency is due, in order of priority, to:

1. The presence of hydrogen bubbles on the surface of the electrode
2. The ionic resistivity of the electrolyte
3. The presence of oxygen bubbles
4. Electrodes distance
5. Membrane (or diaphragm) resistivity

Alternatively, a way to reduce ohmic overpotentials is the introduction of an intermediate electrode so the reduction and oxidation of water occur in successive processes instead of in simultaneous ones. For example, in Japan, Choi et al [92] propose a cell of three electrodes submerged in an alkaline medium: metal hydride (MH), negative; manganese dioxide ( $MnO_2$ ), intermediate; and nickel hydroxide ( $Ni(OH)_2$ ), positive. This idea was developed taking the experience made in other studies of the inclusion of a third electrode in the water splitting thermochemical cycles [93, 94]. The general reactions of each half-cell are



By having an intermediate electrode that separates the reactions, two objectives are achieved: a) higher purity, since the gases are produced in different steps, and b) lower ohmic overpotential, by the use of a thinner separator. In this work, voltage levels below 1.6V were reached at 60°C, resulting in a potentially more efficient production of hydrogen and higher purity.

One way to reduce construction costs is to increase the current density. In order to achieve this goal, it is necessary to counteract the overpotentials so as not to lose efficiency. This is why this particular topic attracts the greatest interest currently. Particularly, as will be presented in Section 4.4, the issues about the materials of the electrodes, catalysts and their structures.

#### *4.3. Impact of electric input fluctuation*

The study of the response to variable input currents is of great interest given the attention caused by the interconnection of electrolyzers with renewable energies. The more direct the connection between them, the higher efficiency can be achieved in the storage of energy in the form of hydrogen. While there are certain investigations that study the response of electrolyzers to the change in the power supply such as a complete interruption or an impulse [95, 96, 97, 98], there is not much information about it [99].

Dobó and Palotás [100, 101] developed a series of experiments to characterize the response of an alkaline electrolysis cell to fluctuations in voltage and current. The electrolytic cell consisted of a closed container filled with 30 wt. % potassium

hydroxide solution with flat plate stainless steel electrodes. In the former case, the cell was fed with a sinusoidal voltage signal with amplitude  $a$  and frequency  $f$  mounted on a direct voltage  $U_{DC}$ . With an amplitude between 0 and 2V, a frequency between 1Hz and 5000Hz and a direct voltage between 1.4V and 2.8V, 6512 experiments lasting 15s were carried out. In each case, the electric power delivered and the gases produced were calculated, the second ones as a function of the pressure change in the cell. The results obtained show that at greater amplitude  $a$  and frequency  $f$ , the efficiency of the cell decreases. In turn,  $U_{DC}$  values are found in which the efficiency is maximum (around 2.2V). Efficiency is defined as

$$\eta = 100Q \left[ \frac{V_m P}{U^0 F} \left( \frac{1}{z_{H_2}} + \frac{1}{z_{O_2}} \right) \right]^{-1},$$

where  $Q$  is the measured flow of gases produced,  $V_m$  is the molar volume of the ideal gases for normal conditions,  $U^0$  is the theoretical decomposition voltage of water,  $F$  is the Faraday constant and  $z$  is the charge number. A degradation of efficiency is obtained with respect to that corresponding to the DC operation of up to 20%. However, there are work zones in which the efficiency drops due to the fluctuation in the input (<2%) can be considered negligible. It is concluded that it is possible to accept fluctuation in the tension but it is recommended to soften the ripple to obtain better results.

In the second case, the cell was fed with several current waveforms (sine, triangle, sawtooth and square) characterized by the direct current  $I_{DC}$ , the root mean square (rms) value  $I_{rms}$  and the frequency  $f$ . In turn, a ripple factor  $r$  is defined as the relationship between the rms value of the  $I_{rms}$  alternating component and the continuous  $I_{DC}$  value, thus comparing the different waveforms.

For frequencies between 1Hz and 10kHz, direct current between 1 kA m<sup>-2</sup> and 5 kA m<sup>-2</sup> and for amplitudes of the alternating component between 0 A m<sup>-2</sup>

to  $I_{DC}$ , 4620 experiments were performed. The results obtained mark a drop in efficiency (similarly calculated as in the previous case) with the increase of the direct current. In turn, there is a decrease in efficiency with the ripple factor (e.g. for  $I_{DC} = 4\text{kA m}^{-2}$  and  $f = 1\text{kHz}$ , the efficiency has a relative decrease of up to 16 % with  $r = 100\%$ ). This is explained considering that the production of gases is directly related to  $I_{DC}$ , while the alternating component increases the power consumed at the same  $I_{DC}$ . Although frequency has a smaller participation, it is highlighted that at higher  $f$  an improvement in efficiency is achieved (e.g.  $I_{DC} = 2\text{kA m}^{-2}$  and  $r = 100\%$ , the efficiency is 48.5% for the case of continuous and it increases to 50% for  $f = 10\text{kHz}$ ).

#### 4.4. *Electrode materials*

The electrodes are usually made of nickel because of its stability. However, it is necessary to counteract the deactivation mechanism. Some solutions are the iron coating [102] or vanadium dissolution [103].

On the other hand, the use of electrocatalysts allows, in addition to stabilizing the electrodes, to reduce the ohmic overpotential. Zeng and Zhang [104] present some examples of anode (Table 6) and cathode (Table 7) materials used in commercial electrolyzers.

In turn, there are those who claim that, for the estimated global capacity of electrolyzers, it will be necessary to dispense with noble metals [116]. Therefore, there are experiences using stainless steel electrodes seeking to improve their electrical efficiency [117]. Besides, Cruden et al [118] compare electrodes based on Nickel with Molybdenum-Resorcinol-Formaldehyde (Mo RF) and other Ni-C-Pt-made electrodes. It is concluded that the proposed Ni-Mo RF can be a replacement for the existing Ni-C-Pt electrodes, the latter being more expensive.

Table 6: Oxygen overpotential of different electrode materials [taken from [104]]

Composition formula	Method	T (°C)	Electrolyte	C(mol dm <sup>-3</sup> )	j (Am <sup>-2</sup> )	$\eta_{oxygen}$ (mV)	Ref.
Ni+Spinel type Co <sub>3</sub> O <sub>4</sub>	Thermo-decomposition	25	KOH	1	1000	235 ± 7	[105]
Ni+La doped Co <sub>3</sub> O <sub>4</sub>	Thermo-decomposition	25	KOH	1	1000	224 ± 8	[105]
MnOx modified Au	Electro-deposition	25	KOH	0.5	100	300	[106]
Li10% doped Co <sub>3</sub> O <sub>4</sub>	Spray pyrolysis	RT	KOH	1	10	550	[107]
Ni	N/A	90	KOH	50 wt%	1000	300	[108]
La <sub>0.5</sub> Sr <sub>0.5</sub> CoO <sub>3</sub>	Spray-stiner	90	KOH	50 wt%	1000	250	[108]
Ni <sub>0.2</sub> Co <sub>0.8</sub> LaO <sub>3</sub>	Plasma jet projection	90	KOH	50 wt%	1000	270	[108]

Table 7: Hydrogen overpotential of different electrode materials [taken from [104]]

Composition formula	Method	T (°C)	Electrolyte	C(mol dm <sup>-3</sup> )	j (Am <sup>-2</sup> )	$\eta_{hydrogen}$ (mV)	Ref.
Ni-Fe-Mo-Zn	Co-deposition	80	KOH	6	1350	83	[109]
Ni-S-Co	Electro-deposition	80	NaOH	28 wt%	1500	70	[110]
Ni50%-Zn	Electro-deposition	N/A	NaOH	6.25	1000	168	[111]
MnNi <sub>3.6</sub> Co <sub>0.75</sub> Mn <sub>0.4</sub> Al <sub>0.27</sub>	Arc melting	70	KOH	30 wt%	1000	39	[112]
Ti <sub>2</sub> Ni	Arc melting	70	KOH	30 wt%	1000	16	[113]
Ni50%Al	Melting	25	NaOH	1	1000	114	[114]
Ni75%Mo25%	Co-deposition	80	KOH	6	3000	185	[115]
Ni80%Fe18%	Co-deposition	80	KOH	6	3000	270	[115]
Ni73%W25%	Co-deposition	80	KOH	6	3000	280	[115]
Ni60%Zn40%	Co-deposition	80	KOH	6	3000	225	[115]
Ni90%Cr10%	Co-deposition	80	KOH	6	3000	445	[115]

Table 8: Main electrocatalyst materials and their current development [taken from [119]]

Material	Activity	Stability	Status
Raney Ni	Sufficient activity	Deactivation after intermittent operation	Commercially used
NiCo, NiFe	High activity, which can be further improved upon alloying with rare earths	Better stability than Raney Ni, but still not optimal	Laboratory applications
NiFe <sub>2</sub> O <sub>4</sub>	Very high activity	Long term stability	Applied in lab-scale electrolysis with polymeric membrane
NiMo	Very high activity	Long term stability	Pyrophoric material: inappropriate for commercialization
(Ni,Co)W	High activity	Unknown	Laboratory applications
Co <sub>2</sub> Si	Very high activity	Unknown	Laboratory applications
Ni <sub>3</sub> N	High activity	Unknown	Laboratory applications

As stated previously, the study of catalysts is receiving increasing interest. As stated by Sapountzi et al [119], the worldwide development of hydrogen production by electrolysis is limited by the search for stable, active and abundant electrocatalysts that allow intermittent conditions. The authors present in Table 8 the main electrocatalyst materials and their current development. Another issue that is being investigated is the use of nanostructures to obtain higher efficiencies or decrease the amount of precious metals needed. Some examples are the deposition of Pd and Ru [120], the incorporation of NiO into a Ni-P matrix [121], the use of Ni nanoparticles on carbon nanotubes [122] and the development of RuO<sub>2</sub>-NiO nanorod arrays on a Ni foam substrate [123]. Table 9 shows the latest developments in the use of nanostructures showing the variety of forms and materials. This list is not exhaustive given the large dispersion.

#### 4.5. Gas-purity dependence

Haug et al [131] developed a series of experiments to analyze the variation of the volumetric concentration of H<sub>2</sub> in O<sub>2</sub> at the outflow of a zero-gap alkaline

Table 9: Comparison of works using nanostructures to obtain higher electrolysis efficiencies

Material	Nanostructure	HER/OER <sup>a</sup>	Activity	Stability	Ref
CoP	Nanosheet@microwire array on Nickel foam	OER	High activity (296mV @100mA)	At least 65h	[124]
NiWO <sub>4</sub>	Nanowire on Ti mesh	Both	Good activity (101mV for HER and 322mV for OER @20mA)	—	[125]
CoTe <sub>2</sub> –MnTe <sub>2</sub>	Hybrid nanowire on Ti mesh	OER	Sufficient activity (310mV @50mA)	At least 60h	[126]
Fe–NiCr <sub>2</sub> O <sub>4</sub> /NF	Fe doped nanoparticles film	OER	Good activity (228mV @20mA and 318mV @500mA)	At least 60h	[127]
CoP <sub>3</sub>	Nanowire array	HER	Sufficient activity (76mV @10mA)	At least 60h	[128]
CoP	Nanosheet on carbon cloth	Both	High activity (52mV for HER and 300mV for OER @10mA)	—	[129]
PtCo–Co/TiM	Ultrafine alloy decorated nanowire	HER	Superior to Pt-based electrocatalysts (70mV @46.5mA)	At least 50h	[130]

<sup>a</sup>Tested in Hydrogen or Oxygen Evolution Reaction

electrolyzer. In this way, states of operation that define the following trends are achieved:

- The reduction in the electrolyte recirculation flow rate allows less impurities.
- A rise in the electrolyte concentration decreases the hydrogen content in oxygen.
- An increase in the temperature of the electrolyte implies less impurities.

It is necessary to clarify that these tendencies are delimited by other relations of commitment, as ohmic overpotential or properties of materials.

Another idea investigated is to know the change of the impurities with three configurations of the circuit. The first and traditional one is the mixing of the



electrolyte recirculation circuits to the cell and the interconnection of both gas separators (mixed). The second one is the independence of recirculations and gas separators, while the third one keeps the recirculation circuits separated but allows the interconnection of the gas separators (partly separated). It is observed that there is an improvement in the purity when passing to separate recirculation circuits while it is not considerable when the gas separators are independent. However, the separation of the recirculation circuits does not allow the equalization of KOH concentrations necessary for the suitable performance of the cell. That is why two solutions that improve the purity are proposed:

- Partly separated method at low current densities (when impurities are higher) and change to mixed method when higher current densities are reached.
- Period cycling of the order of half an hour between the methods partly separated and mixed to achieve an improvement in the purity with respect to the traditional method.

## **5. Discussions**

As presented in the current review, there are interesting alternative methods for the production of hydrogen with virtually zero emissions, among them highlighting the production from biomass and electrolysis. Its biggest disadvantage is the economic cost superior to industrial processes such as the SMR in both construction and operation. It can be seen that these three technologies will coexist in the medium term, waiting for the proportion of SMR to gradually decrease, generating two important niches to be filled by the other two methods: mass production of hydrogen for industry and mobility from biomass, and electrolysis as an energy buffer for renewable sources.

Within the area of electrolysis, a comparative analysis of the various existing technologies was carried out. Advantages and disadvantages of the two commercially available methods have been pointed out, observing opinions of authors in favor of one and against another indistinctly. It is our opinion that both technologies have benefits that lead to their use in different situations: in the case of alkaline electrolyzers, more developed and tested, they are usable as large installations for the stabilization of electrical networks or directly connected to large wind or solar farms. On the other hand, for PEM electrolyzers, with better dynamics and gas quality, it is expected that they can be used as an intermediate energy buffer in industrial plants or at a residential level. In any case, the need to continue research lines to increase their efficiency and reduce their costs is highlighted. Among them is the study of materials for electrodes, electrocatalysts and separators. The other two technologies in development, the SOE and AEM electrolyzers, must overcome the durability barriers in order to compete with the previous ones in the medium to long term.

## **6. Conclusions**

The search for alternative methods of power generation and transport has developed the concept of hydrogen economy. While today hydrogen is obtained mainly from hydrocarbons, new technologies to achieve lower GHG emissions are being developed and consolidated. This paper summarizes the different methods of hydrogen production with emphasis on the current status of alkaline electrolysis. Among hydrogen methods, electrolysis stands out for ease of connection to renewable energies, obtainable purity and their existing but nascent commercialization.

In this paper, current lines of research on alkaline electrolyzers are discussed as it is the ecofriendly-technology with the highest maturity so far. Nevertheless, it requires improvements to be competitive against the production of fossil hydrogen, which means lowering construction and operating costs. The former depends mainly on the materials of the electrodes, so simple or coated non-precious metals are proposed. The later are strongly linked to the efficiency of the system which implies reducing ohmic overpotentials and gases cross-linking of gases. For this purpose, there are several proposals that will need to be deeply discussed and analysed to find the optimum point of operation of alkaline electrolyzers.

The public has to be aware of the importance of reducing the GHG emissions. The hydrogen economy and renewable energies are, until today, the best solution. The development of these technologies needs the coworking between politics, business and science. The aim of this paper is to give a concise and precise idea of the latest progress around the world related to hydrogen economy and, specially, electrolysis in order to encourage the development and investigation in this important matter.

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