

Review

Sustainable Hydrogen Production from Seawater Electrolysis: Through Fundamental Electrochemical Principles to the Most Recent Development

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Abstract: Among the many potential future energy sources, hydrogen stands out as particularly promising. Because it is a green and renewable chemical process, water electrolysis has earned much interest among the different hydrogen production techniques. Seawater is the most abundant source of water and the ideal and cheapest electrolyte. The first part of this review includes the description of the general theoretical concepts: chemical, physical, and electrochemical, that stands on the basis of water electrolysis. Due to the rapid development of new electrode materials and cell technology, research has focused on specific seawater electrolysis parameters: the cathodic evolution of hydrogen; the concurrent anodic evolution of oxygen and chlorine; specific seawater catalyst electrodes; and analytical methods to describe their catalytic activity and seawater electrolyzer efficiency. Once the specific objectives of seawater electrolysis have been established through the design and energy performance of the electrolyzer, the study further describes the newest challenges that an accessible facility for the electrochemical production of hydrogen as fuel from seawater must respond to for sustainable development: capitalizing on known and emerging technologies; protecting the environment; utilizing green, renewable energies as sources of electricity; and above all, economic efficiency as a whole.

Keywords: seawater electrolysis for hydrogen production; electrocatalyst; sustainability; emergent technologies; renewable energy



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1. Introduction

As hydrogen is a carbon-free alternative energy source with several advantages including environmental friendliness and high energy density, it can be used in future energy frameworks. There are many methods for producing hydrogen from water electrolysis that offer both high purity and sustainability. The growing number of scientific reviews on the topic of hydrogen production by the electrochemical splitting of water demonstrates the considerable interest in and financial support for this line of research [1–24]. The hydrogen economy is viewed as a workable solution to the aforementioned issues in light of the rising costs of fossil fuels and increasing environmental degradation. Water electrolysis takes on a special strategic function in this situation [1].

Conventional DC water electrolysis can produce hydrogen. However, the process is not ideal for the environment if the electrical energy for the electrolysis is generated in thermal power plants from fossil fuels due to the release of carbon dioxide. The future of fuel cells is bright, and numerous technologies are being researched globally. Compared with thermal power plants, the amount of carbon dioxide produced during the production

of hydrogen from natural gas for fuel cells can be reduced, although carbon dioxide is still produced. While photo-catalysis is a better method for producing hydrogen, it is still a relatively inefficient process for use in actual applications. Since the cost of energy is declining, by using renewable resources as wind, hydroelectricity, and nuclear power, water electrolysis has recently been considered a method for producing hydrogen [2]. A highly interesting method for producing hydrogen by saltwater electrolysis is the in situ generation of power from waves [25].

A way to lessen environmental pollution caused by power production based on current methods is to produce hydrogen by seawater electrolysis using electricity from local sources and then utilize it in fuel cells.

Two essential components are required for seawater electrolysis to produce hydrogen: cathodes that actively evolve hydrogen during the process and anodes that efficiently develop oxygen rather than chlorine. The most active noble-metallic material for the hydrogen evolution reaction is platinum, but it cannot be used to produce hydrogen on a large scale. Other cathodic materials, such as nickel and several Ni alloys and composite materials, have shown promise for hydrogen generation over the past ten years [21].

High electrochemical reactivity, high energy density, theoretically infinite availability (as long as water can be split), and the combustion byproduct (water) are all benefits of using hydrogen as a fuel in fuel cells.

The need for hydrogen is expected to treble globally over the next five years, and it should also become a cost-effective and sustainable energy source. Hydrogen obtained from different methods, e.g., steam methane reforming, methane pyrolysis, and coal gasification have different effects on environment power systems; the transportation, hydrocarbon and ammonia manufacturing, and metalworking industries all use hydrogen.

Most of the actual hydrogen production, which accounts for around 95% of the 60 million tons produced each year in the context of climate change, is not sustainable, requiring the development of cleaner hydrogen production techniques.

The main review papers address subjects related to hydrogen production from water electrolysis: fundamentals of water electrolysis [3–5,26], the technology of electrolysis cells [2,4,19,24], catalytic electrodes for water electrolysis [1,6,16–18,21], hydrogen production and storage and wastewater valorization [7,13–15,20], renewable energies [6,8], new related technologies [11], and costs and financial considerations [22,24]. The original point of view of this paper is the direct use of seawater as a specific electrolyte, different from pure or alkaline water electrolytes, in order to electrochemically produce hydrogen as a fuel in a sustainable way. The specific characteristics for seawater electrolysis are usually studied and developed by chemists, but the applications are a popular topic in the energy field. From the analyzed articles, only about 20% of the references dealt with seawater, and they were mainly about electrocatalysts for the hydrogen evolution reaction. The found references on energy subject deal with a different type of electrolyte, pure or alkaline water, so they do not offer an integrated view on sustainable seawater utilization.

Since seawater is the largest naturally occurring free resource of water, the fundamental theoretical concepts of water electrochemistry with a focus on seawater electrochemistry will be presented extensively. The most recent trends in electrocatalysts, emerging technology, economics, and environmental impact, as well as the direct use of seawater electrolysis in combination with renewable energy systems for sustainable development will be also discussed.

2. An Overview of Water Electrochemistry

From a broad standpoint, seawater and water electrolysis have very similar electrochemical behavior: At the cathode, reduction reactions (electrons acceptance) take place, while at the anode, oxidation reactions take place (electrons releasing). Figure 1 presents a general scheme of water electrolysis that is also valid for an alkaline electrolyzer (AE). What creates a difference is the electrolyte, which can be water with additional bases, acids, or salts (as in seawater). Depending on the physico-chemical and technological

operating parameters of the electrolysis cell, different secondary reactions may take place at both electrodes depending on the nature of the electrolyte. These reactions may affect the efficiency of the cell, the yield of hydrogen production, and the consumption of raw materials and electricity. The abovementioned issues regarding hydrogen production from water electrolysis lead to the conclusion that this solution is far from an optimum one even though it appears to be a straightforward electrochemical reaction. The subject will remain of high interest for researchers in order to discover the best answer in terms of energy efficiency and costs, even though research and technical advancement in recent years has brought technology extremely near commercial solutions. The electrochemical process called water electrolysis produces extremely pure hydrogen and oxygen. Due to its high purity, electrolytic hydrogen is frequently utilized in the chemical industry, particularly in the energy sector, or for smaller applications such as the semiconductor and food sectors. Hydrogen is also employed in catalytic hydrogenation reactions and ammonia production.

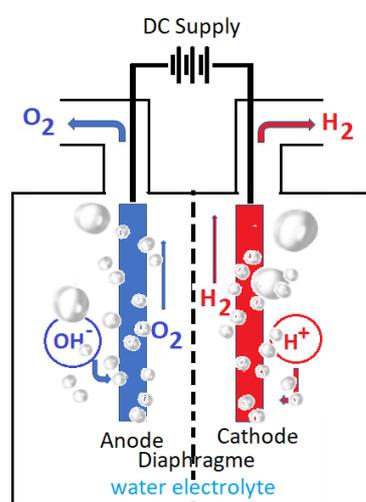


Figure 1. General scheme for water electrolysis.

The need to use pure hydrogen in fuel cells, the low density at standard pressure and temperature, the difficulties of storage, and the possibility of explosion are all drawbacks of hydrogen utilization.

Using electricity, water is electrolyzed and breaks down into hydrogen and oxygen. A direct current (DC) source, an electrolyte, and two electrodes—a cathode and an anode—make up a basic water electrolysis cell.

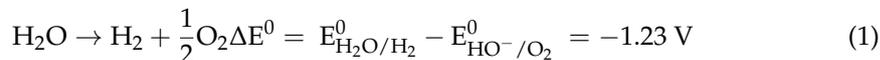
An ion-containing water solution, a proton exchange membrane (PEM), or a ceramic oxygen ion exchange membrane can all be used as electrolyte.

The electrode that is attached to the negative pole of the direct current source is called the cathode. This is where hydrogen is obtained because of the reduction reaction. The electrode that is attached to the positive pole of the current source is known as the anode. It is the location of oxidation reactions and the production of oxygen.

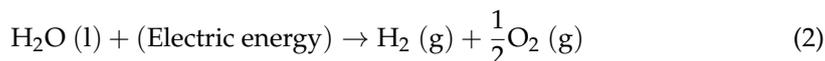
Pure water has a very low electrical conductivity, about $1 \times 10^{-6} \text{ S/cm}^{-1}$, which makes it poorly conductive for electric currents. Under these circumstances, extremely high voltages would be needed to produce hydrogen and oxygen. For this reason, salts, acids, or bases are added to make water more conductive. Due to the increased mobility of hydrogen ions (H^+) and hydroxyl ions (HO^-), acidic and alkaline solutions have higher electrical conductivities than neutral solutions. Although acidic solutions are more conductive than alkaline solutions, the corrosion of metallic components, usually made of steel, causes the increased material consumption of the electrodes, which counts as losses in the process. The electrical conductivity of alkaline electrolytes decreases in time due to the development of carbonates under the influence of carbon dioxide in the air, which results in a 75% reduction in initial conductivity.

When using seawater as electrolyte, it can be used either on its own or in combination with sodium hydroxide.

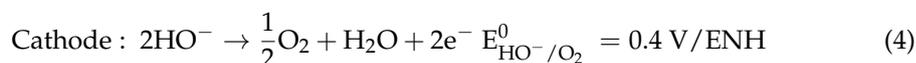
The overall reaction of the cell is also the same, which is the breakdown of liquid water into hydrogen and oxygen gases; although the electrode reactions appear to differ, they are fundamentally the same, specifically the discharge of hydrogen, H^+ , and hydroxyl, HO^- ions:



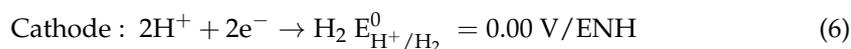
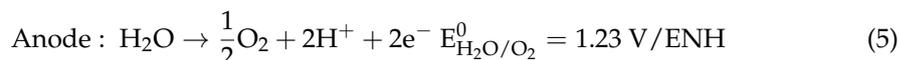
However, the decomposition of water into elements is not a spontaneous reaction at ordinary temperatures, which is why this reaction occurs with external energy input:



In an alkaline environment, the next electrochemical reactions (Equations (3) and (4)) are taking place at the corresponding potentials:



In an acidic environment, Equations (5) and (6) describe electrochemical reactions at the corresponding potentials:



2.1. Thermodynamic Considerations: The Theoretical Voltage of Water Decomposition

The thermodynamic calculation of the water decomposition voltage using the Gibbs–Helmholtz equations leads to the same conclusion, i.e., it confirms the above reactions (Equations (3)–(6)). At 25 °C, the standard heat of the formation of gaseous water is $\Delta H^0 = 57.8 \text{ kcal/mol}$. Since liquid water decomposes at the electrodes, the heat of the vaporization of liquid water, Q_v , under standard conditions (25 °C and 1 atm) must also be considered:

$$-\Delta H = \Delta H^0 + Q_v = 57.8 + 10.52 = 68.32 \text{ kcal/mol} \quad (7)$$

The free enthalpy (Gibbs energy) change in the electrochemical process, ΔG , is given by the difference between the enthalpy change of the chemical reaction and the product between the standard temperature (25 °C = 298 K) and the entropy change, ΔS . Gibbs energy is also equal to the product with the changed sign between the number of electrons z exchanged in the electrochemical process, Faraday's constant (F), and the difference in electric potential between anode and cathode, ΔE :

$$\Delta G = \Delta H - T \cdot \Delta S = -z \cdot F \cdot \Delta E \quad (8)$$

From this equality, ΔE is extracted and calculated as the theoretical voltage difference between anode and cathode necessary for water decomposition, also called the water decomposition voltage:

$$\Delta E = \frac{-\Delta H + T \cdot \Delta S}{z \cdot F} = 1.23 \text{ V} \quad (9)$$

Calculating ΔE from the reversible potentials of oxygen (obtained by oxidation) and hydrogen (obtained by reduction) gives the same theoretical voltage for water to decompose in alkaline (Equation (10)) or acid (Equation (11)) medium:

$$\Delta E_{\text{theoretical}} = E_{\text{ox}} - E_{\text{red}} = E_{\text{oxygen}} - E_{\text{hydrogen}} = 0.4 - (-0.83) = 1.23 \text{ V} \quad (10)$$

$$\Delta E_{\text{theoretical}} = E_{\text{ox}} - E_{\text{red}} = E_{\text{oxygen}} - E_{\text{hydrogen}} = 1.23 - (-0.00) = 1.23 \text{ V} \quad (11)$$

2.2. Balance of Voltage

The real voltage at which the decomposition of water takes place is higher, due to the anodic and cathodic polarizations (η) and the voltage drop on the electrolysis cell, $R \cdot I$ (electrolyte solution, conductors, contacts, diaphragm):

$$\Delta E = \Delta E_{\text{theoretical}} + \eta_a + \eta_c + R \cdot I \quad (12)$$

The type and surface of the electrodes, the nature of the electrolyte, the electrochemical mechanism of the electrochemical reactions, and the temperature all have an effect on the electrode's polarizations and determine the overvoltages (displacements compared with the standard equilibrium potentials). Two elements make up polarizations: a component connected to electron transfer, namely charge transfer polarization, and a component related to mass transfer, namely concentration polarization.

It is desired that the discharge overvoltages of hydrogen and oxygen be as low as possible since they have a significant impact on the voltage balance. The influence of concentration polarizations is lower.

Sandblasted steel cathodes and nickel-plated steel anodes are a straightforward, workable technical solution when considering corrosion resistance and the financial aspect. The creation of electrodes that are up to the task is a constant concern for industry experts, as will be seen in the next sections of this review.

The real water decomposition voltage is measured between 1.6 and 1.74 V, depending on the kind of electrolyte [4]. The voltage drops on the diaphragm, conductors, contacts, and electrolyte solution add up to a significant voltage drop on the electrolytic cell, or $R \cdot I$.

The type and concentration of the electrolyte, the temperature, and the presence of gas bubbles that develop, all affect the voltage drop across the electrolyte. The gases separated at the electrodes (hydrogen at the cathode and oxygen at the anode) during electrolysis form bubbles, which leads to an increase in the voltage drop on the electrolyte. It is well known that when the gas volume reaches 35% of the electrolyte volume, its electrical resistance practically doubles.

2.3. The Electrode Separated Gases

The law of electrolysis, known as Faraday's law, is used to compute the mass of substances separated at the electrodes, i.e., in this case the volumes of produced hydrogen and oxygen.

Any system (conducted, self-conducted, corrosion) can use Faraday's law (Equation (13)), which is expressed as follows: the amount of substance converted in an electrochemical reaction is directly proportional to the electrical charge Q that passes through the system:

$$m = k \cdot Q = k \cdot I \cdot t \quad (13)$$

where m is the quantity of the converted compound [g], and Q is the quantity of electricity passing through the electrochemical system [C], which is equal to the product of the electrolysis time and the electric current intensity. The following relationship provides the electrochemical equivalent, k , and it is specific to the transformed substance:

$$k = \frac{A}{z \cdot F} \quad (14)$$

where A/z is the ratio between the atomic/molecular mass and the number of electrons exchanged during the reaction, z is the number of exchanged electrons, and F is Faraday's number, which is the amount of electricity needed to convert one equivalent-gram of any substance ($1 F = 96,500 C$).

The general statement of the law of electrolysis is produced by replacing the expression of the electrochemical equivalent in Faraday's law:

$$m = \frac{A}{z \cdot F} \cdot I \cdot t \quad (15)$$

The amount of gases separated at the electrodes should rise theoretically by increasing the applied current.

One issue with water electrolysis is that once a higher current is applied, the current density $i = I/S$ increases in relation to the electrode surface. This causes an increase in charge transfer polarizations (discharge overvoltages), which has an impact on the electrical yield and corresponding economic efficiency of the process.

According to industrial practice, the electrolysis cell should be operated within a set of parameters, including a breakdown voltage of roughly 1.82 V and current densities of 300–1000 A/m² [8].

2.4. The Consumed Water during Electrolysis

According to the entire cell reaction, 805 g of water is required for water electrolysis to produce 1 m³ of hydrogen and 0.5 m³ of oxygen under typical circumstances. In reality, more water is used since the released gases have a stripping effect on water. Theoretical considerations are considered when calculating the amount of entrained water, G , in grams related to 1 m³ H₂ under normal conditions:

$$G = 1207 \cdot \frac{P}{(P - p)} \quad (16)$$

where P is the wet gas pressure, [at], and p is the water vapor pressure for an electrolyte concentration at a certain temperature, t , [at].

The gas-stripping effect on water increases with the electrolyzer's temperature. Additionally, it controls the pressure of saturated water vapor and the amount of discharged gases.

Therefore, as the pressure of the gases in the electrolyzer and the concentration of the electrolyte increase, the amount of water drawn will decrease, which in turn affects the price of water vapor. An estimated 850–900 g of water/m³ H₂ is lost through evaporation at a working temperature of 70–80 °C.

Regularly or constantly, demineralized or ion-exchanged distilled water should be added to make up for the water lost through consumption.

2.5. Thermal and Electrical Balance

Under normal conditions (0 °C and 1 atm pressure), the theoretical electric energy usage for 1 m³ of H₂ and 0.5 m³ of O₂ is:

$$W_t = U \cdot I \cdot t = \Delta E_{\text{theoretical}} \cdot Q \quad (17)$$

However, Q can be determined using Faraday's law: $m = k \cdot Q$.

H₂ and O₂ have normal-condition densities of 0.089 g/L and 1.428 g/L, respectively. For a calculation involving 1 m³ of H₂ and 0.5 m³ of O₂, the electric energy will be about:

$$W_t = 2.94 \text{ kWh} \quad (18)$$

Due to the high working voltage, the practical energy consumption W_p is significantly higher. The ratio of required theoretically energy, W_t , to practical energy determines the electrical energy efficiency:

$$\eta_w = \frac{W_t}{W_p} \quad (19)$$

It can be noticed that the electric energy efficiency only depends on the applied voltage on the electrolyzer:

$$\eta = \frac{\Delta E_{\text{theoretical}}}{\Delta E_{\text{practical}}} = \frac{1.23}{\Delta E_{\text{practical}}} \quad (20)$$

The theoretical voltage and the polarizations of the electrodes are included in the practical voltage. The voltage efficiency and the electrical energy efficiency are different because in reality, the electricity consumption is substantially larger, which suggests that some of the current is needed to overcome internal resistances rather than water splitting.

Only 50–60% of the electricity required by an electrolyzer with liquid electrolyte is used for water splitting; the remaining portion is used to overcome internal resistances, which results in additional energy consumption and also overheats the electrolyte. To prevent this, the electrolyzers are cooled so that the process can continue at the ideal temperature.

2.6. Transport and Electrical Resistance

Three key factors contribute to the electrical resistance in a water electrolysis system: the diaphragm, the resistance in the system circuits, and the mass transport stages, such as ion transfer in the electrolyte and gas bubbles covering the electrode surfaces.

Ion transport, heat dissipation, and the distribution and behavior of gas bubbles in the electrolyte are all significantly influenced by convective mass transfer. The mass (ionic) transfer, temperature distribution, bubble size, bubble detachment, and bubble growth rate are all influenced by the viscosity and flow field of the electrolyte, which also has an impact on the current and potential distributions in the electrolysis cell. The concentration of the electrolyte rises as the electrolysis of water proceeds, increasing viscosity. To maintain constant electrolyte content and viscosity, water is often continually fed to the system [3].

2.7. Polarization of the Electrodes

The kinetics of the electrochemical process, or the order of chemical and electrochemical reactions at the level of the metal/electrolyte interface, determines the shifting of the electrode potentials (A—anodic and C—cathodic) from the equilibrium value in Equation (12) and increase the real decomposition voltage. These mechanisms vary based on the characteristics of the electrode and the surface, the temperature, and the electrolyte type. The slowest step, which can be an electric charge transfer, mass transfer, or chemical reaction, controls these mechanisms. Finding the best catalytic electrodes is still difficult even after extensive research due to their complexity, which are specific to the cathodic release of hydrogen or the anodic release of oxygen.

During the operation of the electrolysis cell, the potentials of the electrodes change compared with the value of the equilibrium potentials as follows:

- the cathodic polarization is negative ($\eta_c < 0$), and the net cathodic current density, i_K , is given by the equation:

$$i_K = i_c - i_a \quad (21)$$

- the anodic polarization, $\eta_a > 0$, and the anodic net current density, i_A , is given by the equation:

$$i_A = i_a - i_c \quad (22)$$

Polarization is defined as the difference between the potential at a certain current density and the equilibrium potential: $\eta = \varepsilon_i - \varepsilon_e$.

The anodic (i_a) and cathodic (i_c) partial currents depending on the density of the exchange current, and polarization are given by the equations:

$$i_a = i_0 \exp\left(\frac{\alpha z F \eta}{RT}\right) \quad (23)$$

$$i_c = i_0 \exp\left[-\frac{(1 - \alpha) z F \eta}{RT}\right] \quad (24)$$

Substituting the partial currents from Equations (23) and (24) with the above equations, the Butler–Volmer equations are obtained:

$$i_A = i_0 \left\{ \exp\left(\frac{\alpha z F \eta}{RT}\right) - \exp\left[-\frac{(1 - \alpha) z F \eta}{RT}\right] \right\} \quad (25)$$

$$i_K = i_0 \left\{ \exp\left[-\frac{(1 - \alpha) z F \eta}{RT}\right] - \exp\left(\frac{\alpha z F \eta}{RT}\right) \right\} \quad (26)$$

The Butler–Volmer equations represent the basic equations of charge transfer kinetics. They show the connection between the net current density that produced the polarization and polarization (overvoltage), η .

According to the Butler–Volmer equations, the rate of the charge transfer stage is directly proportional to the density of the exchange current, i_0 , and it is in an exponential relationship with η , the charge transfer coefficient α , and $(1 - \alpha)$.

2.8. Main Water Electrolysis Cell Types

2.8.1. Alkaline Electrolyzer

Alkaline electrolyzer (AE) are the most used and simple electrochemical systems for water electrolysis. Utilizing strong electrolytes with high ion mobility, such as sodium or potassium for positive ions and hydroxide or chlorides for negative ions, the conductivity of the solution increases. Water molecules migrate to the cathode during electrolysis via diffusion as they are consumed, while hydroxide ions move to the anode by migration (movement caused by an external electric field) and diffusion as they are consumed. As shown in Figure 1, a diaphragm divides the two compartments of the cell, the anode and cathode, and collects the produced gases: hydrogen at the cathode and oxygen at the anode. Because they have much higher conductivities and less corrosion impact than acid electrolytes, concentrated potassium hydroxide solutions are typically used. Nickel is frequently utilized as the basis for electrode materials because of its low cost and high activity.

2.8.2. PEM Electrolyzer

PEM electrolyzers (Figure 2) are distinguished by their compactness and extremely straightforward manufacture [4]. Water electrolysis using a proton exchange membrane (PEM) operates on a straightforward premise. Water is broken down into protons and molecular oxygen at the anode during electrolysis. The water flow removes oxygen, and the electric field's influence causes protons to travel toward the cathode. They are converted to molecular hydrogen there. The electro-osmotic flow is the solvation atmosphere created by water molecules that each proton carries [3,4].

Thus, the membrane performs the multiple roles of electrolyte, electrode, and gas separator. As a result, the membrane needs to possess specific physico-chemical characteristics, such as: high ionic conductivity, which favors proton migration and lessens ohmic drop; inability to conduct electricity to prevent short circuits; stable chemical composition; low oxygen and hydrogen permeability; good pressure resistance and mechanical and dimensional stability; and good thermal stability in an operating range of 80–100 °C.

The following variations can be noted in comparison with a liquid electrolyte [3]: because the membrane's anionic charges are fixed, there can be no concentration gradient.

The bubble gas formation and evolution are connected with the geometry (disposal and state) of electrode surface. A better type of electrolyzer design is based on a horizontal disposal of the electrodes. Gas is released through the back of the electrodes. Depending on the type of ions being transported and the characteristics of the membrane (thickness, mechanical resistance, conductivity), the water content of the membrane varies.

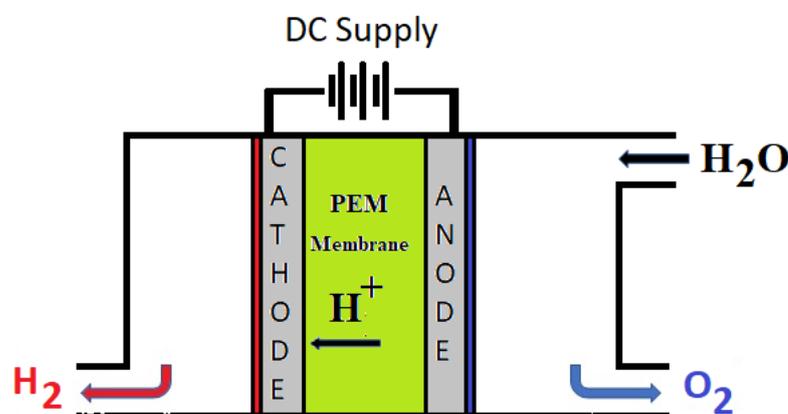


Figure 2. PEM electrolyzer.

2.8.3. Solid Oxide Electrolyzer

A solid oxide electrolyzer or a solid oxide cell (SOC) is a device in which electrolysis takes place at high temperatures. As temperature rises, the solid oxide electrolyzer can operate with high efficiency. Solid oxide fuel cells are a new technology under development. They are electrochemical devices that can function reversibly in the electrolysis mode. The solid oxide electrolyzer reduces water vapor to H_2 in the process [3,18,26–28].

The most established and well-known cells use an alkaline electrolyte; they are commercially available, have a lifespan of two to three decades, and require the least expensive catalyst. The electrolyte is a corrosive liquid, and they use lower current densities, operational pressure, and gas purity. When compared with electrolyzers using an alkaline electrolyte (which have an efficiency of 52–90%), PEM electrolyzers have an efficiency of about 90–95%. However, they require a noble metal catalyst, are more expensive concerning the membrane and other components, and have the same issue with corrosive electrolytes.

Many recent studies provide instructive comparisons between different water electrolyzers from the perspectives of electrochemical, electric, economic, and other factors, such as energy performance or hydrogen production [4–8,18,26,28].

If we weigh the benefits and drawbacks of each technology, we may conclude that PEM electrolyzers and cells with liquid electrolyte are the most suitable for producing hydrogen from seawater electrolysis [4,5,18–21,23,26,28,29]. The main advantages are accessibility and the lower costs of material and operating costs.

3. Newest Trends in Seawater Electrolysis for Hydrogen Production

3.1. Specificity of Seawater Electrolysis

The commercial production of hydrogen and related products using seawater electrolysis is theoretically viable and has great promise as a green process. Seawater electrolysis has the same basic principles as those of water electrolysis but also a bit more because of the chemical composition based on salts such as sodium chloride. The goal is to create hydrogen from saltwater, and there are three basic ways to accomplish this:

- Electrolysis to produce alkalis, hydrogen, and oxygen.
- Electrolysis to produce alkalis, hydrogen, oxygen, and chlorine.
- Electrolysis to produce hydrogen and sodium hypochlorite ($NaClO$).

The most practical method of seawater electrolysis appears to be the second one. Given a large number of target products, the process in this scenario can be carried out

at reasonable costs. However, in this instance, the chlorine must be a by-product that can only be released into the environment in a secure manner. One way to achieve this is by converting the chlorine present in anodic gases into hypochlorite. This last substance, the hypochlorite, is a common antibacterial agent used to disinfect drinking water or wastewaters. More than 70 elements are dissolved in saltwater, but only 6 of them account for more than 99% of all dissolved salts; they are all present as ions. The main seawater composition is presented in Table 1 [25,30].

Table 1. Seawater main composition (ppm) [25,30].

Chloride (Cl ⁻)	Sodium (Na ⁺)	Sulphate (SO ₄ ²⁻)	Magnesium (Mg ²⁺)	Calcium (Ca ²⁺)	Total Dissolved Salts TDS
19,345	10,752	2710	1295	416	35,000

The total dissolved solids on which artificial seawater formulas are based are estimated to be around 35,000 ppm, of which sodium chloride makes up roughly 30,000 ppm. Surface waters are typically saturated due to wave action and exposure to atmospheric carbon dioxide, whereas deep ocean waters are typically undersaturated in terms of carbonates. This saturation will have an impact on the deposition of calcium and magnesium salts during corrosion, when cathodic protection is applied, and when seawater is electrolyzed.

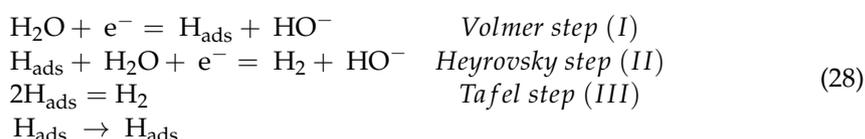
With a few modifications that are detailed below, the reactions at the electrodes in the case of natural or artificial seawater electrolysis are largely comparable with those of water electrolysis.

The cathodic reaction, hydrogen evolution reaction (HER) at the cathode, complies with Equation (1):



A thin layer of calcareous deposits, primarily made of CaCO₃ and Mg(OH)₂, accumulates at the cathode surface during seawater electrolysis. According to the following equations, Ca²⁺ and Mg²⁺ ions precipitate as a result of the local pH increase caused by the hydrogen evolution reaction near the cathode surface. Scale deposits that have accumulated on the cathode keep expanding if they are not eliminated. The growth rate increases as the water temperature rises, water hardness increases, and flow velocity increases. Ca²⁺ and Mg²⁺ ions are better able to mass transfer to the cathodic surface when flow velocity increases. Scale eventually fills the spaces between the electrodes, and they are completely blocked.

Numerous investigations of nickel-based electrodes have focused on the hydrogen evolution reaction (HER). Atomic hydrogen is an intermediate product in alkaline solutions, as can be seen in the following scheme [9,31] (Equation (28)):



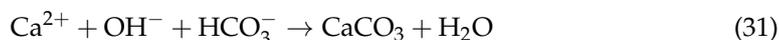
The primary electron transfer step involving the adsorbed hydrogen on the electrode surface (H_{ads}) from an H₂O molecule is the Volmer step (reaction I). The Heyrovsky step or/and the Tafel step, which results in the production of the H₂ gas, come next. The presence of the Heyrovsky step (reaction II) indicates that the H₂ molecule was created by the simultaneous reduction of the H₂O molecule and the desorption of adsorbed hydrogen. The Tafel step (reaction III) shows that two nearby adsorbed hydrogen atoms combine to produce the H₂ molecule. The adsorption of a portion of atomic hydrogen (H_{ads}•) may change the catalytic characteristics of a nickel surface layer. Combinations of Volmer and Tafel steps or Volmer and Heyrovsky steps with one step acting as a rate controller are the postulated mechanisms for the HER.

At the anode, an oxygen evolution reaction (OER) and/or a chlorine evolution reaction (CIER) can occur in accordance with the following equations:



Toxic chlorine must not evolve from the anodes used in seawater electrolysis, and the anodes must also be highly effective and long-lasting. The majority of the typical anodes for seawater electrolysis have been modified to create chlorine, as is widely known. Commercial seawater electrolyzers that effectively convert anodically produced chlorine into hypochlorite solution are evidence of the chlorine evolution's dominance.

A thin layer of calcareous deposits, primarily made of CaCO_3 and $\text{Mg}(\text{OH})_2$, accumulates at the cathode surface during seawater electrolysis [31]. According to the following equations, Ca^{2+} and Mg^{2+} precipitate because of the local pH increase caused by the evolution hydrogen reaction near the cathode surface:



First electrodes known to produce oxygen in seawater electrolysis with a high level of efficiency were anodes coated in manganese oxide [31–33].

In many places, especially in hot, arid locations, freshwater has historically been a rare resource. Equipment for water purification and desalination is required while building an electrolytic water system in order to pretreat saline and low-grade water. The flow of input fluid and outflow air streams, gas regulators, and thermal management devices are all complicated setups that distinguish practical electrolyzers from basic laboratory systems. Even without accounting for associated investments in transportation and maintenance, the deployment of more water purification devices unavoidably comes at a prohibitive cost.

The economic efficiency of purification/desalination can be significantly increased by removing pretreatment systems. The creation of appropriate electrode catalysts with stable and selective electrocatalytic activity in seawater is a crucial step in the deployment of direct seawater electrolysis.

However, it is well known that seawater is a complex solution with a high concentration of different salts (up to 3.5%), in which a variety of competing redox processes and dramatic pH changes cause catalysts to degrade. Thus, a macroscopic understanding of direct seawater electrolysis is first covered in this review, and the distinction between electrolysis in seawater and pure water is then made clear. However, based on the potential electrochemistry involved in this process, we will focus on efficient methods for the logical building of electrocatalysts with better selectivity and stability for both electrodes [17].

Major electrocatalytic reactions currently in use, such as the hydrogen evolution reaction, concentrate on the production of a single target chemical, which is hampered by intense competition between reactions occurring at the same electrodes or by high energy barriers between reactions occurring at the opposite electrodes. Co-electrolysis is a promising new technique for reducing energy consumption and producing other added chemicals in the same electrolytic system [34].

A revolutionary method for producing hydrogen while using less energy is to replace the OER with thermodynamically more advantageous electro-oxidation processes. This method also adds other functionality such as electrosynthesis. Combining saltwater reduction with thermodynamically advantageous hydrazine oxidation is one of the effective options. As a result, the hydrazine oxidation reaction has a huge potential for producing hydrogen at much lower voltages than OER, which translates to reduced power use. Unfortunately, hydrazine poses a serious threat to human health because it is highly carcinogenic and toxic. The advantage for saltwater electrolysis is that it avoids the well-known issues

with chlorine chemistry without reducing the electrolysis current or hydrogen-producing efficiency [35].

3.2. Electrocatalysts for Hydrogen Production

Electrochemical energy conversion and storage methods need electrocatalysts in order to build sustainable and ecologically friendly energy systems. Many different electrochemical processes are generally used in the systems that use electrochemistry for energy conversion and storage; they emit less carbon dioxide and have high energy densities. The electrocatalyst's most important attributes for widespread use are its efficiency and affordability.

Out of the numerous electrocatalyst examples available, we selected some examples to highlight the primary electrocatalyst types recently reported to be employed for water electrolysis, with a focus on saltwater electrolysis. The energy efficiency of the electrolysis system improves with using electrocatalysts. Numerous transition-metal-based compounds have proven to be excellent electrocatalysts [1,9,16–21,29,31–101] and they are presented in Table 2.

Table 2. Transition-metal-based electrocatalysts for different water electrolysis cells.

Type of Electrocatalyst	References
Pt-based	[1,9,16–20,40,41,57,58,98]
Ni-based	[1,16–21,29,31–33,36,38,43,48,57–59,62,66,68,69,75,82,91,92]
Fe based	[1,16,18–20,29,44,48,49,53,55,57,58,66,81,98,101]
Mo based	[16,17,19,20,43,44,50,57–60,77]
Co based	[1,16–20,35,40,47,50,52,57,58,61,80,96]
Cr based	[9,17,32,33,57,58]
Ti based	[17,21,57]
Ru based	[9,17–19,58]
Ir, based	[17,18,20]
W based	[17,18,80]
Selenides	[1,16–20,40,85,90]
Phosphides	[1,16–20,53,71,72,76,80,81,87,93,94,100]
Carbides/C based	[1,16–20,36,37,42,46,47,52,65,78–80,84,86,90,96,97,99]
Nitrides	[9,16–20,34,41,44,60,61,65,70,77,84,90,97]

Transition metal compounds (oxide, sulfide, selenide, phosphide, carbide, and others) are among the many electrocatalyst candidates being investigated due to their potent electrocatalytic activity. The mechanisms of various electrocatalysts vary. Electrocatalysts are crucial for boosting reaction rates because they make it easier for reaction intermediates to be converted and reduce resistance. The most sophisticated electrocatalysts for HER (Pt), OER (Ir/Ru oxide), and ORR (Pt) are noble metals, but their high price and limited supply prevent them from being widely used in industry.

Several commercial electrodes built from Pt(Mo₂C)-produced catalysts exhibit high catalytic activity for the hydrogen evolution reaction (HER) in 0.5 M sulfuric acid solution, even at relatively low platinum loadings [37]. Commercial electrodes built of Ni and Ti mesh work well and provide excellent cathode materials, and they are less expensive than electrodes based on Pt [38]. Other materials, which are less expensive than Pt-based electrodes and have good performance, offer ideal electrode materials for widespread application.

Another important element to consider is the thermodynamic stability of the electrodes, also known as corrosion stability, since the anodic and cathodic spaces are always subject to highly corrosive conditions regardless of the electrolyte's pH.

The electrodes' price must be, of course, the next justification. They may be constructed from expensive and inexpensive materials, corrosion-resistant metals, and alloys, including noble metals.

The materials used to make the electrodes employed generally in water, but especially in seawater electrolysis, must meet certain requirements. The electrodes in seawater must have electrocatalytic properties for both main reactions taking place at the electrodes: the hydrogen evolution reaction (HER), the most studied, and the oxygen evolution reaction (OER). This will reduce polarizations and implicit voltage drops on the electrolysis cell. Other secondary electrochemical reactions that may occur at the electrodes include: CIER (chlorine evolution reaction); COR (Cl^- oxidation reaction); GOR (glycerol oxidation reaction); ORR (oxygen reduction reaction); HzOR (hydrazine oxidation reaction); UOR (urea oxidation reaction); MOR (methanol oxidation reaction).

In Table 3 are listed the possible electrochemical reactions that could appear at seawater electrolysis.

Table 3. Possible electrochemical reactions at seawater electrolysis.

Reaction	Type	References
Main	HER	[17,29,31–33,36,39,41,44,49–51,53–57,59,63,64,66,67,73,77,78,81,87,95,96,98,101]
	OER	[17,29,36,40,41,50,53–57,59,64,66,67,73,101]
Secondary	CIER	[81]
	COR	[98]
	GOR	[91]
	ORR	[52]
	HzOR	[77]
	UOR	[88]
	MOR	[90]

It is to be noticed that there are three types of research studies: studies on the electrocatalyst materials, studies on electrolysis cell performance, and studies that involve both aspects. Table 4 displays the results of research studies on suitable seawater electrocatalysts for HER/OER used in the electrolysis process that were carried out between 2018 and 2022.

Different electrochemical and nonelectrochemical investigation techniques, specifically structural investigation, simulation, and calculation, were employed to explain the electrocatalytic activity of the catalyst used at seawater electrolysis. A schematic classification of the primary electrocatalyst investigation techniques utilized for hydrogen production by water and seawater electrolysis is shown in Figure 3.

The most popular electrochemical techniques include chronopotentiometry (CP), linear sweep voltammetry (LSV), cyclic voltammetry (CV), and electrochemical impedance spectroscopy [EIS].

For instance, the HER in synthetic seawater on Ni [31] and 18Cr-10Ni stainless steel [32,33] electrodes was studied using steady-state polarization curves and electrochemical impedance spectroscopy. As seen by the Tafel behavior, charge transfer regulates the hydrogen evolution reaction in artificial seawater in the form of the Nyquist and Bode impedance graphs [31–33,43].

Table 4. Electrochemical parameters of some electrocatalyst and electrolyzers performance in seawater mentioned in studies published during the period 2018–2022.

Electrocatalyst	Electrode Reaction	Overpotential, mV	Current Density, mA/cm ²	Tafel Slope, mV/Decade	Cell Voltage, V	Cell Current Density, mA/cm ²	Stability, h	Faradaic Efficiency, %	Ref.
NiMoS	HER	-	14,6	-	1.9		100	17.9	[39]
MNiNS, Ni/Pt-C, Ni/Ir-C	OER, HER	197–524	100	58.8–308.2	1.8	48.3	12		[41]
Co-Se	OER, HER	268–280	100	40.4–61.4	1.8	10.3	12		[40]
(h-MoN NPs)/BNCNTs	HER	78	10	46					[42]
Ni-Mo alloys	HER	103–900	44,571	105–158				86.7–100	[43]
NiMoN@NiFeN, Ni/IrO ₂	OER	277–542	100–500	58.6–86.7	1.6–1.72	400	48		[44]
MXene, carbide	HER						225	98	[46]
NiFe- OH/ Pt					1.6	200	100		[48]
S-doped Ni/Fe (O)OH	HER	300–398	100–500		1.83–1.95	500–1000			[49]
Ni ₃ S ₂ /Co ₃ S ₄ (NiCoS), (NiMoS)	OER, HER				2.08	800	100	17.9	[50]
Co/Co ₃ O ₄ @C	ORR								[52]
(CaFeO _x FePO ₄) oxide	OER	710	10				10		[53]
FeOOH/ β-Ni-Co-OH	OER, HER				1.57–2.02	20–1000	378		[54]
Ni-Fe-OH	OER, HER					0.4–1000		11.9	[55]
PtM (Cr, Fe, Co, Ni, Mo)/Ti	OER						172		[57]
Pt-Ru-M (Cr, Fe, Co, Ni, Mo)	OER						172		[58]
NiMo/Ni, NiMoO ₄	OER, HER				1.563	10			[59]
Mo ₅ N ₆	HER								[60]
Ni-N ₃	HER	102–139	10			200	14		[34]
NiCoN, NixP	HER	165	10						[61]
NiCo@C	HER	200	1.34		2.53	310	60–140		[62]
MnO ₂	OER					1000	4200		[64]
NiFe-LDH	OER	260	100	43.4			20–50		[66]
NiFe-LDH	OER				2.4	800	12	94	[29]
MnO ₂ -based Electrodes	OER							47.2–100	[67]

Table 4. Cont.

Electrocatalyst	Electrode Reaction	Overpotential, mV	Current Density, mA/cm ²	Tafel Slope, mV/Decade	Cell Voltage, V	Cell Current Density, mA/cm ²	Stability, h	Faradaic Efficiency, %	Ref.
Ni(OH) ₂	OER	340–382	100		1.65		80		[73]
MoNi/NF	HER, OER	219	100	40–120		1000		100	[77]
MFC-N,O doped C	HER	161	10	97.5			76		[78]
CoP-WP/rGO	HER	96–208	10	36–125		1000	30		[80]
FeCo-Ni ₂ P, MIL-FeCoNi	HER	201–310	100–1000	29–45		>500	100		[81]
Ni ₂ P-FeP	HER	89	10		1.68	100	90		[87]
Fe-Ni(OH) ₂ /Ni ₃ S ₂	OER	269	10	46			27	95	[95]
Co/GCFs	CIOR, HER	181.8	10				10–20	98	[96]
Pt-NiFe PBA	HER, OER	29–210	10		1.46–1.48		12	100	[98]
Graphite					3–4.5			25.48–71.99	[17]
Co, Ni/C	HER								[47]
NiCo/MXene				0.7–1.0	0.7–1.0	500	140		[35]

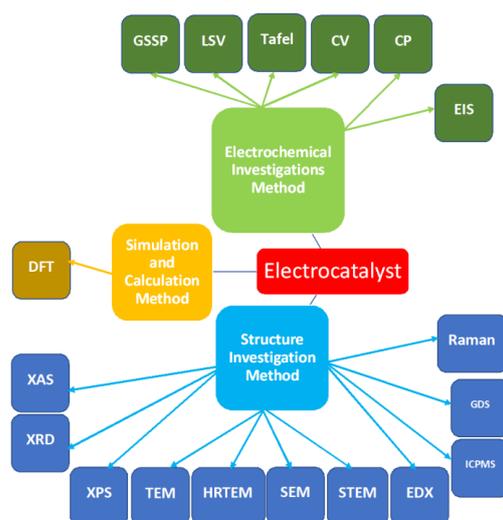


Figure 3. Schematic classification of the primary electrocatalyst investigation techniques utilized in the electrolysis of freshwater and seawater to produce hydrogen.

Investigating in the area of surface chemistry to determine the crystal structure of the electrodes includes spectrophotometric techniques such as X-ray diffraction (XRD); X-ray photoelectron spectroscopy (XPS); scanning transmission electron microscopy (STEM), dark field scanning transmission electron microscopy (DF-STEM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), scanning electron micrography (SEM), energy-dispersive X-ray spectroscopy (EDX), Raman spectroscopy, and X-ray absorption spectroscopy (XAS) or glow discharge spectroscopy. These techniques are used not only to explain the properties of electrocatalyst surface but also for the understanding of the catalyst's electrochemical processes and performance [10].

The design of new, highly efficient catalysts would be accelerated significantly by the use of calculations, like density functional theory (DFT) or other machine learning strategies. Thus, a deeper understanding of the underlying relationship between catalyst structure and catalytic performance would be made possible.

A classification of the main investigation methods used for electrocatalysts characterization is presented in Table 5.

Table 5. Investigation methods for characterizing the properties of water/seawater electrocatalysts.

Method Type	Method Name	References
Electrochemical	Chronopotentiometry (CP)	[29,73,75]
	Linear sweep voltammetry (LSV)	[35,40–44,49,55,61,66,69–76,78,80,81]
	Cyclic voltammetry (CV)	[55,66,67,74,76,80,95,96]
	Electrochemical impedance spectroscopy (EIS)	[31–33,41,43,46,69,71,74,77,80,95,96]
Structure investigation	X-ray diffraction (XRD)	[10,16,41,43,44,67,72,74–81,96]
	X-ray photoelectron spectroscopy (XPS)	[41,44,66,72–78,80,81,87,95–97]
	Scanning transmission electron microscopy (STEM)	[40,41,44,81]
	Dark field scanning transmission electron microscopy (DF-STEM)	[44]
	Transmission electron microscopy (TEM)	[35,40,41,44,73–76,81,87,95–97]
	High-resolution TEM (HRTEM)	[40,41,44,66,73–76,81]
	Scanning electron micrography (SEM),	[16,35,43,44,55,66,69,71–74,76–79,87,95–97]
	Energy-dispersive X-ray spectroscopy (EDX)	[43,44,73,75,76,78,96]
	Raman spectroscopy	[10,52,72,78,95]
X-ray absorption spectroscopy (XAS)	[10,34]	
Glow discharge spectroscopy	[79]	
Calculation & simulation	Density functional theory (DFT)	[9,10,34,39,60,70,75,95]

The provided information shows that there are many different electrocatalysts and that they are all promising ways to find materials suitable for HER/OER efficiency in seawater electrolysis. As was evident, there are numerous calculations and research techniques employed in in situ determinations. The task for the coming decades will be to identify the best electrocatalytic materials for the electrolysis of seawater to produce hydrogen, as well as solutions that combine all current demands for energy efficiency, affordability, sustainability, and environmental friendliness, to make the technology commercially viable. The type and design of the electrolysis cells, the volume of hydrogen produced, the cost and energy effectiveness, and the environmental impact are all equally significant.

3.3. Economic Considerations

Water electrolysis is gaining popularity; however, under a scenario of climate change mitigation, supplying 24% of the energy demand with hydrogen will require vastly more renewable electricity output. To power electrolyzers in this scenario, more electricity would be needed than is currently produced globally from all sources combined to more than 30 terawatt-hours. The infrastructure for manufacturing, storing, and transporting goods would also require significant investment. Freshwater affordability and accessibility, as well as the availability of renewable energy, will be vital. Priorities for water electrolysis research include finding water resources, locating water sources, figuring out how to use the produced oxygen, and improving process efficiency [12].

Future low-carbon energy systems may rely heavily on energy storage to maintain a balance between intermittent supply and demand. The interest in converting renewable electricity by electrolysis into storable fuel is driven by the need for energy storage. Storing renewable energy in chemical bonds, particularly hydrogen, is appealing due to their high energy density, elemental abundance, long-term storability, potential low costs, and capacity to transfer renewable electricity to the chemical industry or to the heat and transportation sectors. However, there are potential impediments to investing in water electrolysis, including high initial costs and uncertainty about future cost and performance improvements [9].

For example, a fundamental obstacle to industrial-scale hydrogen production is the high running cost for even pure water electrolyzer. Combining HER with other thermodynamically more advantageous and beneficial electrooxidation reactions could lower costs by using less energy [10].

Any hydrogen generation pathway's effectiveness is assessed by dividing the output energy by the input energy. By taking into account the costs of feedstock, applied energy, electrocatalyst materials, capital expenditures, and operating expenses, the cost-effectiveness of a process can be evaluated [13,14]. Similar to any other techno-economic analysis, a SWOT (strength, weakness, opportunities, threats) analysis for the hydrogen production from water should be conducted taking into account both the cost and an analysis of sustainable development goals. Economic factors such as investment and production costs, as well as technological advancements and their effects on the environment and society as steps for commercial, sustainable, and industrial uses, all have an impact on the marketing of hydrogen produced by water electrolysis (Figure 4).

Investing costs and learning rates for PEM and alkaline electrolyzers from the 1990s to 2017 and beyond were evaluated in a recent study of the literature. Inflation was taken into consideration in the data collection. Costs associated with water electrolysis were significantly reduced during the study period, particularly for PEM technology. The expenses of investment will also be impacted by automation, greater cell areas seen in mass production, marketing, and technology development [22].

Fortunately, the price of electricity produced by solar PV (photovoltaic) and wind continues to drop, and it will not be long before this renewable energy source's extremely cheap price becomes accessible [24]. As it is known the price of energy is connected with the resource disponibility but also affected by market demands and financial and

geopolitical interests. But in any technology which evolve, the price will be lower for the same performance, which means that somehow the prices drop in time.

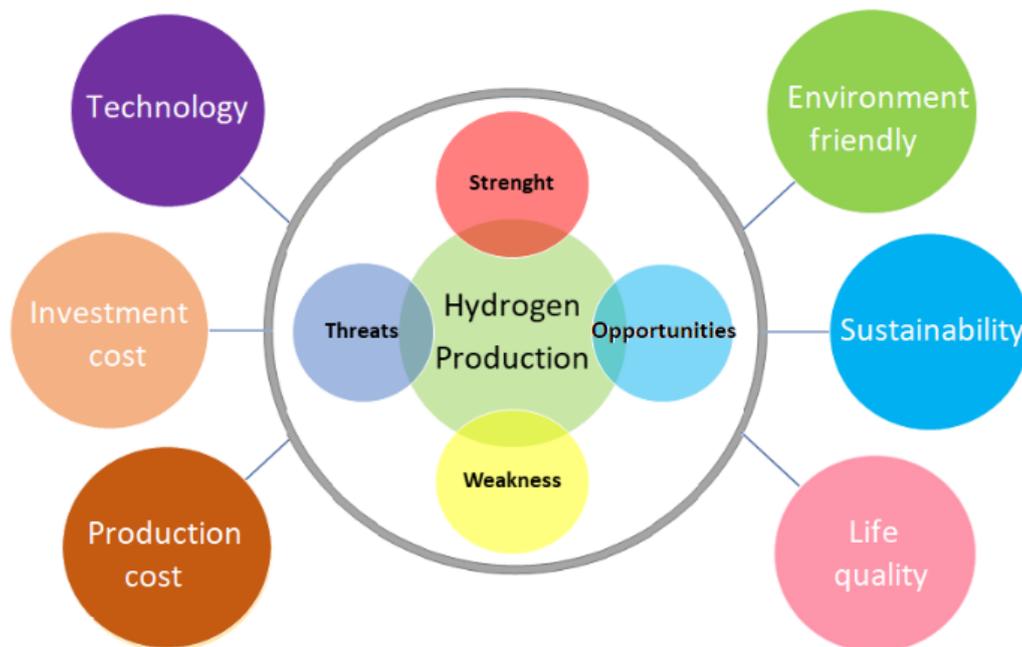


Figure 4. Scheme of the technical and economic analyses of the hydrogen production.

It is necessary to store energy in the case of renewable energy sources with variable availability. Storing hydrogen in the form of a chemical compound and its subsequent use can lead to lower costs [102].

In order to have a correct view on hydrogen production technology, it might be necessary to compare the cost of a seawater-based electrolysis facility with other systems, e.g., a trigeneration system was proposed to produce freshwater, hydrogen fuel, and electricity using a classic coal power plant [103].

Beginning in 2020, hydrogen production was planned for Hawaii's fuel cell-powered buses used for public transportation. This example demonstrates how coupling hydrogen production systems with other load centers can be advantageous for both parts under conditions of high renewable penetration. When analyzing the economics of hydrogen production, it is crucial to take the system's fluctuating efficiency into account. The current electricity pricing structure has a significant impact on the cost of hydrogen production and the most effective manner of operation [104].

A recent study used the MATLAB software to evaluate and optimize the exergy and exergoeconomic performance of a geothermal energy plant. Various scenarios are offered in order to identify the examined system's optimum states [105].

In Pakistan, a study was run on the potential of wind energy to produce renewable hydrogen for cost-effective green production. As a creative project idea for large-scale hydrogen use that took into account the expenses for hydrogen are electricity and storage costs, the use of wind and renewable hydrogen energy for green economic production was offered [106].

A techno-economic model was developed to evaluate and compare the fuel yields, energy efficiency, carbon efficiency, and minimum selling price of two processes that include integrated biomass gasification, electrolysis, and syngas biomethanation with combined heat and power recovery [107].

A pertinent analysis of the costs of a hydrogen production facility based on the electrolysis of seawater must take into account any other classic or new method, such as the utilization of methane gas or biomass [108].

Two technological systems, Dish–Stirling and power towers, that produce electricity, for a reasonable cost, using concentrated solar energy were the subject of a survey and economic analysis. To determine the total cost of producing and storing energy in this hybrid system as a function of investment cost (I), operation and maintenance cost (O&M), interest price, amount of energy produced, and levelized cost of electricity are computed [109].

Using co-electrolysis, adding other substances in water electrolyzer led to a gain by obtaining other commercial chemical products or by destroying them in order to achieve the environment requirements at the same price. Examples of co-electrolysis are the electrochemically generation of both hydrogen and hydrazine [35,77], urea [71,88], ammonia [76], or glycerol [91].

The total cost of seawater electrolysis technology for producing hydrogen must account for all costs associated with the electrolysis cell and its electrical, chemical, and electrochemical performance as well as other costs associated with transporting and storing reagents and electrolysis products and also complying with regulations given that the hydrogen gas produced is highly flammable. Unfortunately, despite the abundance of fundamental research studies and the acceleration of expansion, there are now just a few viable, real-world solutions. Efficient and commercial technologies are just getting started.

3.4. Environmental Considerations

Hydrogen is a versatile, clean, and adaptable energy source that is well-known for its zero emissions, high energy efficiency, and recyclable energy resources. It is one of the current innovative alternative energy resources seeking to tackle the global energy depletion and greenhouse gas emissions. The use of hydrogen in industry and transportation has made it a highly potent instrument [25,63,91]. Hydrogen is a carbon-neutral transportation fuel on land.

For hybrid water splitting, it is strongly recommended to develop bifunctional catalysts based on earth-abundant materials for cost savings, simplicity, and practical applications. It is crucial to create new oxidation processes, particularly the electrooxidation of pollutants and biomass (such as sulfides and halides), in order to produce hydrogen while simultaneously reducing the risks with minimal energy use. To separate the anode and cathode products in this situation and choose the membrane that is controlled by the applied electrolyte, membrane-based practical systems are needed.

It is possible to produce efficient bifunctional electrodes that are an energy-efficient combination for both hydrogen generation and environmental improvement through sewage treatment by using a low-cost electrocatalyst in urea-assisted hydrogen generation [71].

To become carbon neutral, it is essential to develop water splitting powered by renewable energy for environmentally friendly hydrogen production. However, the anodic oxygen evolution reaction's (OER) slow kinetics significantly hamper the effectiveness of conventional pure water electrolysis. This makes the energy-saving hydrogen production method of hybrid water electrolysis, which is significant in furthering the global sustainable energy system, a viable alternative to OER in favor of other thermodynamically more favorable oxidation reactions. Using catalytic electrodes, which are also used for ammonia oxidation and water splitting, is a cost-effective and sustainable technique to produce pure hydrogen. In order to conserve electricity and preserve the environment, [76], both water/seawater and other substances are involved in electrochemical reactions. Some examples are the oxidation reactions of: hydrazine [35,77,81], glycerol [17,91], urea [71,88], methanol [90], and ammonia [76]. Hydrogen generation has also employed wastewater from biodiesel and olive mills [17], and electrochemical wastewater treatment and biohydrogen production with the help of different bacteria were investigated. Extensive reviews present a great variety of microorganisms that can be used in the microbial cells that are present in the effluents of various agro-industries or sewage [11–14,38].

Renewable energy is necessary for both environmental protection and energy security. Hydrogen from water electrolysis holds great promise for the future since it has the potential

to reduce carbon dioxide pollution, increase profitability for wind power plants, and use renewable electrolyzer facilities [106]. Water electrolysis is the process used to create hydrogen, and life cycle analysis was used to compare the effects of several hydrogen-generation methods, including steam methane reforming, methane pyrolysis, and coal gasification [12,108]. The production of green fuel using a hybrid concentrated solar system and electrolysis has been shown to be environmentally responsible and sustainable [109].

In order to prevent the negative impacts of fossil fuels, new clean techniques of hydrogen production must be thoroughly examined and investigated. Furthermore, hydrogen needs to be produced sustainably in order to be a more eco-friendly and sustainable energy source. In recent years, there has been an increase in interest in using hydrogen as a novel and environmentally beneficial fuel. The green hydrogen society that is being developed on the basis of wastewater successfully ensures effective wastewater utilization and is thought of as a forward-thinking project for a sustainable future.

3.5. Emergent Electrochemical Technologies for Seawater

The literature reveals numerous innovative methods for producing hydrogen through more affordable pathways using some interesting, rapidly evolving technology. Seawater electrolysis, electrophotolysis, bioelectrolysis, and thermochemical electrolysis are electrochemical-based technologies that are now in use and for which there are already sufficient data about energy efficiency [13,14]. Table 6 briefly summarizes their key attributes, including energy input, energy efficiency, technology, and raw materials [11–15,17,38,39,107,110–115].

Table 6. Electrochemical based technologies for hydrogen production.

Involved Process	Electrolyte	Energy Input	Technology	Energy Efficiency (%)	References
Electrolysis	Water	Electric	AE	62–82	[13–15,39,110,111,113]
	Brine		PEM	67–84	
	seawater		SOC	75–90	
Electrophotolysis	Water seawater	Photonic Electric	Photoelectro- chemical	0.5–12	[13–15,39,110,111,113]
Bioelectrolysis	Biomass	Bioenergy Electric	Microbial Nitrogen fixation	70–80 10	[11,13,17,38,112,115]
Thermochemical Electrolysis	Fuels Water Metals Hydrides	Heat Electric Chemical reaction	Plasma reforming Redox reactions	9–85	[12,13,107,114]

Using various bacteria, microbial fuel cells and microbial electrolysis cells—also known as “bioelectrochemical assisted microbial reactors” [13,14]—can be used for practical wastewater treatment and biohydrogen production. Some examples could be microbes from domestic or municipal wastewater [11] or anodophilic microorganisms [38]. They are environmentally friendly and could be considered a renewable energy source as the production of wastewater is continuously produced in usual municipal and industrial activities.

A sustainable energy supply strategy for the future is made possible by photochemical systems, which use water splitting to transform solar energy into stable, transportable chemical fuels such as H₂ or carbon-based fuels. Solar–photovoltaic–electrochemical systems, one of the evolving systems, have seen a recent trend in technology development.

The optimized techniques will guarantee greater energy efficiency for photochemical systems. PV–EC (photovoltaic–electrochemical) systems combine electrocatalytic hydrocarbon production with photoelectric conversion (HER and CO₂R–CO₂ reduction). The solar cell, which is connected in series through the DC–DC conversion zone with EC modules

to match the current and voltage well in order to achieve the highest energy conversion efficiency, converts solar energy received from the sun into electricity in the PV–EC system. The use of this technology is restricted by the higher hardware costs and difficult fabrication process of PV–EC systems [14,39]. The fast development of photovoltaic electrolysis (PV–EC) should focus on high solar-to-hydrogen efficiency based on inexpensive semiconductors in order to maintain its role in the technological race, whereas photoelectrochemical water splitting is regarded as a promising method of solar hydrogen production [15].

There are many other possible technologies of the future included in Table 6, but some of them could not be applied for the direct use of seawater due to its specificity (simultaneous release of oxygen and chlorine at the anode and dissolved salts). One example is thermochemical electrolysis, i.e., molten carbonate electrolyzers, in which there has been increased interest in recent years as a method of obtaining not only fuel hydrogen but also other gases with industrial potential. Table 7 lists the emergent technologies based on electrolysis that can use as an electrolyte both water or seawater: anion exchange membrane (AEM), membrane electrolyzer, unitized regenerative technology—based on one unit for both reversal electrolyzer and fuel cell and battolyser technology—and fully charged batteries that produce hydrogen are listed as the most current and promising emergent electrochemical technologies that could lower costs and increase the efficiency of hydrogen production [14].

Table 7. Related references for emergent technologies for seawater electrolysis.

Emergent Technology	References
Anion exchange membrane (AEM)	[14,17,73,108,115]
Membrane electrolyzer	[12,14,116,117]
Unitized regenerative technology	[14,118,119]
Battolyser technology	[12,14,120–122]

Figure 5 schematically shows the most suitable emergent technologies for obtaining hydrogen from seawater.

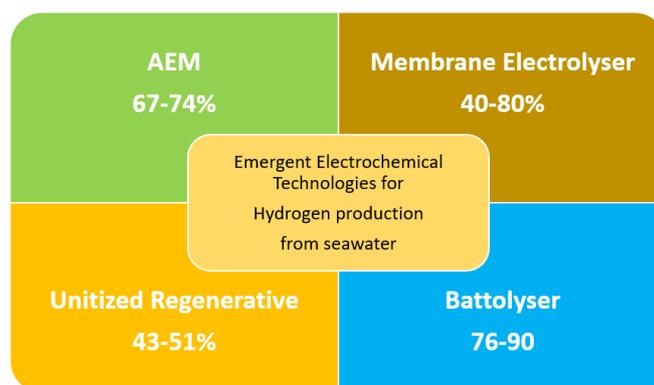


Figure 5. Efficiency of emergent electrochemical technologies suitable for hydrogen production from seawater.

3.6. Renewables Energies for Seawater Electrolysis

A potential source of renewable, clean energy is hydrogen generation. Natural gas reforming, which uses sizeable amounts of nonrenewable energy and concurrently creates the greenhouse gas carbon dioxide, is how industrial hydrogen is mainly produced. Therefore, it has been a priority for researchers worldwide to create effective and affordable electrochemical water splitting systems. For the production of H₂, using green energy systems to lower overall energy consumption is more crucial. Different green energy systems can effectively reduce external power consumption by capturing and converting

energy from the environment for water splitting. Recently, a number of environmentally friendly hydrogen production methods have been developed, i.e., water splitting powered by photoelectrode devices, solar cells, thermoelectric devices, triboelectric nanogenerators, pyroelectric devices, and electrochemical water-gas shift devices. It is crucial to focus more on the development of green energy systems in order to produce pollution-free energy, which will make it possible to realize the entire process of hydrogen generation with cheap, clean, and sustainable energy conversion [20].

Solar energy, geothermal energy, wind energy, microhydropower, and wave energy are all suitable for water and seawater electrolysis in order to obtain hydrogen (Figure 6). Due to the irregularities in the availability of renewable energy sources including solar, wind, small hydro, geothermal, and ocean throughout the year, the field of hybrid renewable energy systems has experienced significant growth. In response to increased demand, a number of studies on the architecture, operation, dependability, and optimization of hybrid renewable energy have been published recently. Table 8 presents the main renewable primary sources of energy that could be sustainably used for seawater electrolysis [10,24,25,39,55,63,104,105,109,110,116,118,123–135].

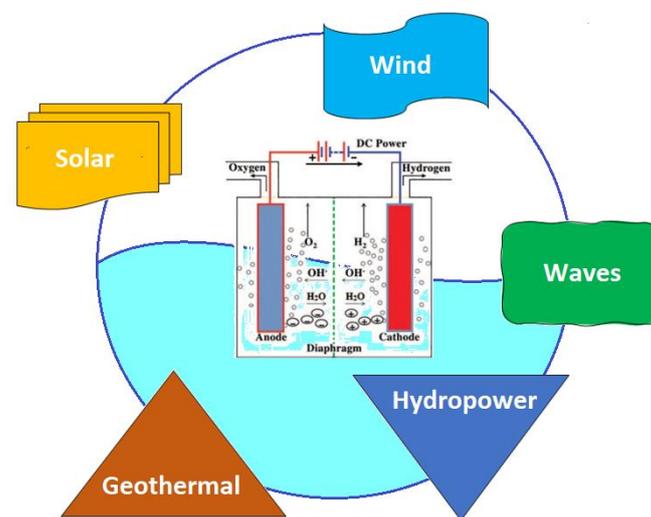


Figure 6. Renewable sources of energy for hydrogen production from seawater electrolysis.

Table 8. Main renewable sources of energy that could be sustainably used for seawater electrolysis.

Type of Renewable Source	References
Solar energy	[10,24,25,39,55,63,104,109,110,118,123–129,131,132]
Wind energy	[25,63,104,116,125,126,128,130,132]
Geothermal energy	[25,63,105]
Microhydropower	[132]
Waves energy	[25]
Hybrid renewable energy	[10,25,63,105,123,127–135]

For example, a microfluidic electrolyzer was developed as a green technology solution for the continuous production of hydrogen using photovoltaic cells: hydrogen and oxygen were separated in a Y-shaped electrolyzer [123]. Another possibility for further reducing the cost of electricity is to link the electrolyzer with a solar system in order to implement hybrid water electrolysis on a large scale and for commercial purposes. An examination of the energy and exergy of hybrid systems should offer more understanding [10,25]. A proposed integrated multigenerational system is thermodynamically examined with an emphasis on energy and exergy [63]. This sustainable multigenerational system, which

consists of six subsystems and is based on geothermal, solar, and wind renewable energy sources, produces electricity, hot water, heating, and cooling in addition to hydrogen [63].

Without using any additional fuel, seawater electrolysis powered by sea waves, and its direct conversion to electrical energy could run constantly and produce hydrogen [25].

Higher levels of solar generation would be good for both the electrolyzer loads and the research campus load, according to analyses of the impact of increasing solar penetration on the cost of hydrogen production [104]. The Weibull distribution function (WDF) and the Angstrom–Prescott (AP) equation for hydrogen generation were used to analyze the wind and solar energy potentials in Iran [125].

A cutting-edge energy system that uses a low-grade organic Rankine cycle, an absorption chiller, and a low-temperature PEM electrolyzer to make hydrogen proved to be a useful energy storage material. According to calculations, the system's overall energy and exergy efficiencies are 41 and 50%, respectively [105].

Consider the trend in the rising percentage of variable wind and solar plants in the EU for a brief evaluation of green energy projects (Italy, France, Spain). The energy content of green hydrogen at the exit of electrolyzers (power to gas) fueled by renewable electricity is anticipated to cost roughly EUR 1.2/kg between 2030 and 2050. When compared with the same price for the 2021 EU gas market penalization for CO₂, the cost of hydrogen content of energy at the exit of electrolyzers is estimated to be around EUR 36/MWh in 2050. Although the compression, transport, and distribution of hydrogen present significant challenges [128]. Hydrogen proves to be a true answer when compared with the new challenge of the year 2022, the new economic–political contests (war, economic and social catastrophe). Less than 1% of hydrogen was found to be produced by hybrid energy systems in a recent Chinese study [129]. The prices are estimated to range between USD 9.55 and USD 11.67 per kilogram in a Korean Monte Carlo simulation case study on a system based on a battery energy storage system and a freestanding solar photovoltaic (PV)-powered alkaline water electrolyzer (AWE) [131].

Hybrid isolated power systems with a type-2 fuzzy PID system were proposed for storing energy: a wind turbine generator with a diesel engine generator, a PV–microhydropower system (MHP), and a polymer electrolyte membrane fuel cell [132].

The modeling and optimization of electrochemical processes for water and wastewater treatment processes were possible using artificial intelligence (AI) techniques such as artificial neural networks, support vector machines, adaptive neuro-fuzzy inference system, genetic algorithms, and particle swarm optimization [133].

The experimental tests showed that seawater electrolysis to produce hydrogen is a reasonable procedure with one requirement: the electric energy must be sufficient and reasonably priced to balance the high consumption. Environmental scientists agree that the integration of renewable energy is the best course of action for improving energy security and environmental performance by ensuring continuous access to clean and green energy [106,135].

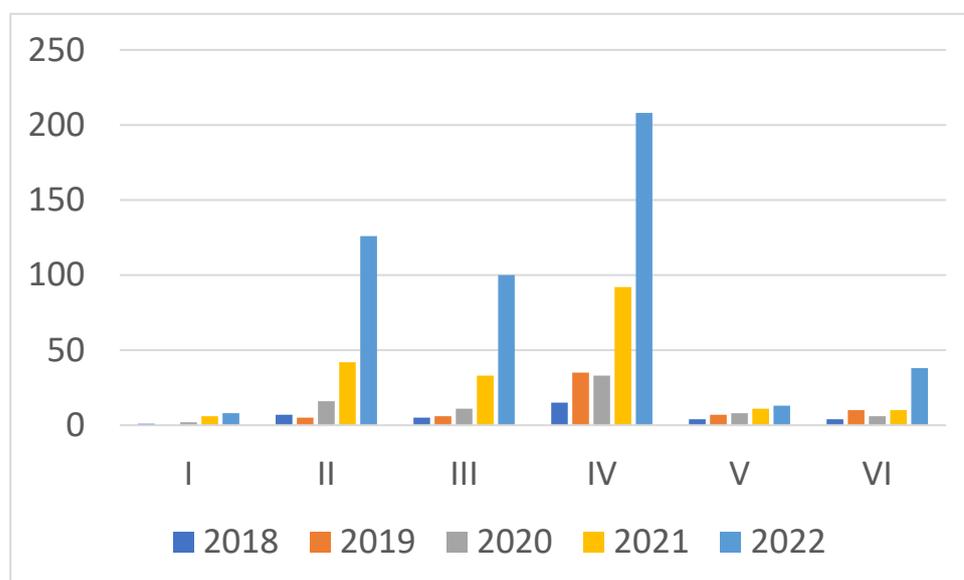
4. Conclusions

For this review two types of selecting the papers criteria have been used. At the first search, based only on “seawater and electrolysis”, over more than 2000 references have been founded for last 5 years, but introducing specific criteria this number of references was decreased. Main criteria for selecting papers for this review was obtaining hydrogen, only from liquid seawater electrolysis, not from pure or alkaline water, using catalytic electrodes, especially for hydrogen evolution reaction, because H₂ is the main and most important product of seawater electrolysis. It has been performed a statistical analysis of the studied literature, focusing on the searches (I–VII) in the database <https://link.springer.com> (accessed on 10 October 2022) using the different keywords related to Table 9.

Table 9. Search key words for studies published during the period 2018–2022.

Search No.	All the Words	Exact Phrase	Number of Found Articles 2018–2022
I	Electrocatalyst and seawater and splitting	seawater splitting	37
II	electrocatalyst and seawater and splitting	seawater	196
III	Electrocatalyst and seawater and hydrogen and production	hydrogen production	155
IV	seawater and electrolysis and hydrogen and production	hydrogen production	383
V	seawater and electrolysis and hydrogen and production and waste	hydrogen production	43
VI	seawater and electrolysis	seawater electrolysis	103
VII	seawater and electrolysis	-	2370

Search I, with the smallest number of references, can be found in Table 9 (the number of additional article took in consideration also “salted water” and “overwater”—meaning all pH water). The results of searches I–VI, represented in Figure 7, underline the constant growth of interest both for seawater electrolysis and production of hydrogen, as an alternative energy source, in the last 5 years (2018–2022). Another aspect of the search that can lead to seemingly different results is the use of synonymous words such as water “electrolysis” and water “splitting”.

**Figure 7.** Evolution of scientific articles number related to hydrogen production from seawater electrolysis by search of different key words (I–VI).

It is also desirable to emphasize that the human factor is still decisive in selecting the references as correctly as possible, sometimes the keywords appear only once in the body text, and the article deals with a related topic. For example, in the Vth search, out of the 43 references, only 12 works were original research articles, the rest were book chapters, and out of the 12 only 10 were really related to hydrogen production. Although many of the references are from journals in fields related to energy, it is noticeable that there is more concern for obtaining hydrogen, as the source of energy, than for finding solutions to meet the challenges related to the environment and sustainability, emphasizing once again the role of the market, the costs and the general interests of the people.

It is obvious the increased interest, we could say exponentially because of the new geopolitical situation of year 2022, which is not yet over, for the production of hydrogen, as one of the most promising energy sources of the future.

A second criteria of selecting papers was the sustainability of using seawater electrolysis: the connection between hydrogen production from seawater and aspects to take into consideration: the environment protection, the utilisation of local renewable sources of energy, what emergent technologies of water electrolysis are also suitable only for seawater, without forgetting to deal with the costs. This criteria was more particular, that's why only some of newest (2018–2022) and representative (some older than 2018) papers have been included in the selected references, considered necessary by the authors for understanding the complexity of sustainable hydrogen production through seawater electrolysis. The selection included papers also related to pure or alkaline water electrolysis, which are also suitable for seawater electrolysis. A promising tool for improving the energy system is the hydrogen economy. For fuel cells, hydrogen is also excellent. Because it can use any energy source other than a greenhouse gas, the concept is renewable because hydrogen is produced using the water electrolysis technology (with the help of renewable or nuclear energy). Avoiding the significant corrosion loss brought on by acid electrolytes or by using potassium hydroxide, seawater electrolysis is a very promising solution, as is using other novel electrodes, especially cathodic materials with high activity, availability, and lower cost, as catalysts in addition to noble metals. Commercial electrodes that are reasonably priced could be viewed as cost-effective alternatives are a key development in large-scale applications in industries like hydrogen or biohydrogen generation.

Since seawater makes up 97% of the earth's surface, it is seen to be an endless resource, and fresh water is becoming more and more valuable. Direct use of seawater in electrolysis systems can be a feasible and practical strategy for coastal dry zones and offshore large-scale hydrogen outputs when cost reduction is considered.

Between the two types of water, pure/alkaline water and seawater there are similarities and differences, which can be significant both from the point of view of the electrochemical mechanism, design of the electrolyser, final costs, even to the possibilities of being included in the emergent technologies.

Electrolysis of seawater is a subject of growing interest, but still a difficult option for solving the global energy issue because of some limitations, listed below.

At the cathode, during the electrolysis of seawater, the same reaction takes place mainly as during the electrolysis of pure water (with/without the hydroxide addition), namely the release of hydrogen. On the other hand, at the anode, the situation is different in seawater: in addition to the reaction of releasing oxygen, there is a competing reaction of releasing chlorine (due to the content of chloride ions in seawater), which leads to a mixture of gases, oxygen being difficult to separate. An environment with high corrosive potential is formed in the anodic space. This anodic second reaction [136] is less studied than the others reaction. The specificity of seawater electrolysis it is reflected in the design of the electrolyser, meaning: the electrolyte, the type of electrodes and the constructive solution. This paper wants to emphasize the role of interdisciplinarity in the development of this technology. Seawater is the most widespread and cheap electrolyte and there are so many remarkable results for the electrochemical efficiency of the process. There is a gap between the advanced results of electrochemical research and cell design and their practical use in energy facilities with a pertinent assessment of energy and economic efficiency. This is why, this review intend to be a useful tool for those who intend to develop an accessible technology for obtaining hydrogen, specifically from seawater and which meets the criteria of sustainability.

The present paper is focused on the identification of the main aspects of a sustainable technology for the hydrogen production from seawater, without exhausting the subject. Adjacent topics less addressed are for example: utilisation of dedicated PEM electrolysers for seawater, which have some difficulties in being advantages methods (i.e., stability, degradation of materials) [137], possibility of using electrocatalyst in order to suppress the

secondary anodic reaction, namely chlorine evolution [136] or developing new hydrodynamic Computational Fluid Dynamics (CFD) designs for a better electrolyser efficiency, i.e., using Laser Doppler Velocimetry (LDV) method [138].

Some of the promising emergent technologies which involve hydrogen production, are not suitable for using liquid seawater electrolysis, i.e., nuclear power or molten carbonate fuel cell (MCFC). Electricity for direct seawater electrolysis could come from any other primary sources of energy (fossil fuels, biomass, nuclear energy), but this review focus on green renewables. Nuclear energy, as this technology become safer and more accessible, is probably the cheapest source of energy and also CO₂-free. However, nuclear energy cannot be considered either renewable or risk-free at this moment. There is also no need of high values of temperature or electric current to run seawater electrolysis. Molten carbonate cells could not be operated with raw seawater because of the chlorine formation and the corrosion potential developed by chloride and hypochlorite ions.

In this review, it is highlight the fact that theory, research experiments, and practice are all necessary for the development of future, viable, technologies for producing hydrogen directly from seawater. The article also wants to remind that a reliable and accessible technology is the fruit of interdisciplinary research, and in this case, electrochemistry is a part of a sustainable development.

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