

# Advancements in Solar-Driven Seawater Electrolysis for Green Hydrogen Production: Innovations, Challenges, and Future Prospects

Muhammad Atif Daniel Aziz<sup>1</sup>, Norazlianie Sazali<sup>2,3,4\*</sup>, Fatin Ayu Kartika Mohd Suzaki<sup>5</sup>, Afdhal Junaidi<sup>6</sup>, Kumaran Kadirgama<sup>3,7</sup>

<sup>1</sup>Faculty of Manufacturing and Mechatronic Engineering Technology, Universiti Malaysia Pahang, 26600, Pekan, Pahang, Malaysia;

<sup>2</sup>Faculty of Mechanical and Manufacturing Engineering, University Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia

<sup>3</sup>Centre of Excellence for Advanced Research in Fluid Flow (CARIFF), University Malaysia Pahang Al-Sultan Abdullah, 26600, Pekan, Pahang, Malaysia.

<sup>4</sup>Mechanical Engineering Department, Sepuluh Nopember Institute of Technology Kampus Keputih Sukolilo, Surabaya 60111, Indonesia

<sup>5</sup>Faculty of Chemical and Process Engineering Technology, University Malaysia Pahang Al-Sultan Abdullah, 26300 Gambang, Malaysia

<sup>6</sup>Department of Chemistry, Faculty of Science and Data Analytics, Institut Teknologi Sepuluh Nopember, Sukolilo, Surabaya 60111, Indonesia

<sup>7</sup>Faculty of Mechanical and Automotive Engineering Technology, Universiti Malaysia Pahang, 26600 Pekan, Pahang, Malaysia

**ABSTRACT** - Solar-driven seawater electrolysis has become one of the attractive options for sustainable hydrogen production by utilizing plentiful seawater with the energy of natural solar. However, using seawater itself poses complicated electrochemical issues such as chloride-induced corrosion, competition for chlorine evolution reactions, catalyst instability, and low energy efficiency in actual marine environment. This review highlights significant advances in solar-based seawater electrolysis technologies such as photovoltaic-driven electrolysis and photoelectrochemical technologies, photocatalytic processing methods, vapor-phase water splitting systems and several others. Specific focus is placed on the reaction mechanisms targeted at seawater types, relevant performance indices, and material design strategies with a view to increasing reaction selectivity and operational persistence. The merits and shortcomings of various system designs are compared to emphasizing the achievements and challenges. Finally, future studies for the stability of catalyst, integration of systems, and realistic testing scenarios are discussed to facilitate development of scalable and environmentally friendly hydrogen production from seawater.

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## 1. INTRODUCTION

Hydrogen is widely considered to be the most important energy carrier for the long-term decarbonization of the global energy system, as it has a high gravimetric energy density and it does not produce carbon emissions during use [1]. At present, most industrial hydrogen is made by steam methane reforming (SMR), which is thought to use a lot of energy and release a lot of carbon dioxide, which is less useful for the transition to green and sustainable energy [2]. Saltwater electrolysis with solar energy-electrochemical conversion or photo-assisted splitting is an efficient method of producing hydrogen without power from outside sources [3]. A lot of nanostructured catalysts are being developed to speed up reactions and to increase the efficiency of solar-to-hydrogen conversion [4]. Sun-based hydrogen is a renewable energy source and has a high energy density of 142 MJ/kg (about three times higher than gasoline) and only makes water when burned [5]. Fossil-based feedstocks are still the main source of hydrogen, even though they have a big carbon impact. This shows how important it is to find the so-called green hydrogen technologies that can help us achieve carbon neutrality [6]. Some of the technology paths that have been examined for this change are photoelectrochemical (PEC) systems, photovoltaic-powered electrolysis (PV-EC), and photocatalytic seawater splitting [7]. Seawater is a vast supply, but actually splitting it into hydrogen and oxygen is more difficult than freshwater due to its high chloride ions and other dissolved cations ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) which can kill catalysts or accelerate the breakdown of electrodes [8]. Water electrolysis is one of the most common ways to produce green hydrogen from renewable energy. In contrast, conventional electrolysis has to rely on freshwater for its supply, so we are concerned about the scalability of electrolysis and the safety of the water supply in dry areas [9].

Recent progress in surface regulation and engineering design for photoelectrodes is in the field of lowering the chlorine evolution reaction (CER) and improving control in saline situations [10]. Photocatalytic vapor splitting is a cheap and safe way to reduce salinity even further. It uses water vapor as a feedstock and doesn't contact corrosive liquid seawater [11]. The majority of water on Earth is in the ocean. This means that seawater is a virtually infinite natural resource, a resource that would be very useful for solving most of the freshwater crisis in the world [12]. Developers are working to make corrosion-resistant electrodes with passivating layers that are made of polyanions to make them more corrosion resistant and therefore less susceptible to chloride ions and make oxygen evolving more selective [13]. These saline

components create complex electrochemical states that make the process less efficient and less stable over time. To make sure the system works in real-world applications, parameters and material design must be optimized by computing [14] in order to be reliable in practice.

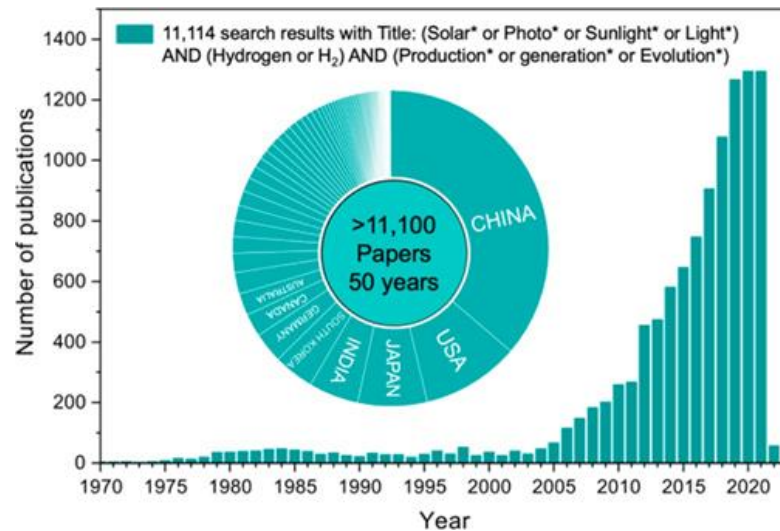


Figure 1 Number of publications searched by the words (Solar\* or Photo\* or Sunlight\* or Light\*) and (Hydrogen or H<sub>2</sub>) and (Production\* or Generation\* or Evolution\*) [13].

## 2. MATERIALS AND METHODS

### 2.1 OVERVIEW OF SOLAR-DRIVEN SEAWATER ELECTROLYSIS

Solar-driven saltwater electrolysis can be understood in two ways, direct seawater splitting and indirect seawater-to-hydrogen conversion [6][21]. Seawater is the feedstock for photocatalytic, photoelectrochemical, or photovoltaic-assisted electrolysis systems that convert sunlight into chemicals to create hydrogen [3, 6, 15]. In indirect systems, seawater is first converted into clean vapor or condensed water before hydrogen is made. This protects catalysts and electrodes from corrosive ions in seawater [15, 21]. This difference is crucial since the choice of pathway impacts the stability of the catalyst, the selectivity of the reaction, the complexity of the system, and growth over time [6][21].

Photocatalytic seawater splitting is often considered the simplest way to do things; it is believed it can produce hydrogen directly from light without the need for an extra circuit [6][15]. However, its application is still limited by low solar-to-hydrogen efficiency as well as hard gas separation, poor use of visible light, and the lack of long-term stability in salty waters [6][10][15]. The direct photocatalytic seawater splitting is also sensitive to side reactions, fouling of the surface, and catalyst deactivation due to chloride. This makes it less effective in real saltwater [10][12]. The PEC seawater splitting is a more regulated pathway since the light absorption and electrochemical charge separation takes place at photoelectrodes, so the reaction management is better than with particle photocatalysis [3][6][17]. If photoanodes and photocathodes are integrated properly, PEC systems can also reduce the external bias needed [6, 17]. Nevertheless, the effectiveness of PEC in seawater is limited by photoelectrode corrosion, chloride oxidation, surface recombination, and after long-term use, the durability of the PEC system is low [12]. These limitations suggest that PEC systems are technically attractive but are still highly challenging to be used in practical maritime settings [6].

Photovoltaic-assisted electrolysis (PV-EC or PV-E) is the most advanced solar-driven way right now since the photovoltaic unit and the electrolysis are not connected, which makes it possible to improve each part of the system on its own [6][15]. The decoupled architecture is more flexible, easier to scale up, and can leverage previously commercialized photovoltaic and electrolysis technologies to achieve a relatively high total solar-to-hydrogen efficiency [1][6][15]. When saltwater is directly used in a PV-assisted electrolysis system, PV assisted systems still experience a lot of issues with electrochemistry, which include chloride corrosion, the formation of chlorine or hypochlorite, catalyst degradation, and the need for selective and durable electrocatalysts at industrial current density [12][24]. PV-assisted electrolysis is the most advanced technology, but it is not yet applied directly to seawater because anode protection, catalyst selectivity, and corrosion resistance need to be greatly improved [12][24].

Indirect photothermal–photocatalytic vapor splitting is an alternative method. Saltwater is turned into water vapor by solar thermal evaporation, and hydrogen is made from the vapor [15][21]. This avoids the direct contact of liquid seawater with the catalytic surface. It is also less likely to encounter chloride attack, salt scaling, and fouling problems with liquid-phase saltwater electrolysis [21][24]. Vapor-fed systems can also be more flexible in relation to temperature management, mass transport design, and system-level isolation between hydrogen generation and seawater treatment [21]. But this path also brings new issues with it, such as slow photocatalytic vapor-splitting rates, heat loss during evaporation processes,

the need for better materials for photothermal and photocatalytic processes, and better structures for vapor transport [6][21]. At this point in time, none of the solar-powered seawater electrolysis pathways are meeting the requirements for high efficiency, robust stability, corrosion resistance, low cost, and to be used in the industry [6][15]. Photocatalytic systems are easy to use but are not very effective. PEC systems provide better control, but they also do not have the best stability in terms of material instability. PV-assisted electrolysis is the most advanced, but the electrolysis process is still prone to chloride issues. Vapor-phase systems reduce contact with corrosive liquids, but they have low conversion efficiency and are difficult to set up [6][21][24]. The current research trajectory is moving towards a more unified understanding of the interplay of material selection, electrode stability, system architecture, and operating circumstances in practical seawater-to-hydrogen performance [16][21][25].

## 2.2 Real Seawater Composition and Electrochemical Implications

Real seawater is a chemically complex electrolyte composed not only of water and sodium chloride, but also of dissolved ions, suspended solids, organic matter and microorganisms that can affect electrochemical hydrogen production [10][12]. Besides  $\text{Na}^+$  and  $\text{Cl}^-$ , seawater typically has  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{SO}_4$ ,  $\text{HCO}_3$  and  $\text{CO}_3^{2-}$  species, which can affect ionic conductivity, interfacial reactions and surface adsorption and electrode stability in a process [12][21]. Real seawater is composed of different kinds of dissolved ions and is not just purified water, but even simple simulated seawater solutions, so the results of model electrolytes cannot be easily translated to real surface conditions [10][21]. Chloride ions are the most important in terms of selectivity and corrosion in the anode [12][24] from an electrochemical standpoint in alkaline water and in the anode in water.

In alkaline water, oxygen is a faster chemical process than chlorine and, in a strong enough or weakly selective or stressed anode, the chemistry of chloride can still occur in anode chemistry and the catalyst surface [12][23][24]. In other words, a high level of catalytic activity is not sufficient, but the anode must also ensure selective oxygen evolution while curbing hypochlorite or chlorine side reactions [12][23]. As a result, the electrochemical properties of seawater systems depend on catalyst composition and operating pH, applied potential, and surface reconstruction throughout the system [12][24]. Besides chloride, divalent cations such as  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  are also problematic for the system because they can form hydroxides or other insoluble deposits at the electrode surface when alkaline is used [12][21].

Therefore, natural seawater gives rise to chemical and physical instability that is not present in laboratory-processed electrolytes [21]. Another important aspect of real seawater composition is that it is related to catalyst degradation and electrode lifetime [12][23]. Aggressive ionic species can cause surface corrosion, structural disorder and dissolution of unstable active phases, particularly when anodic polarization is extended. In photoelectrochemical and photocatalytic systems, this is even more critical because the catalyst or photoelectrode must also be sensitive to light irradiation, the transfer of an interfacial charge, local pH gradients and salt-induced surface stress [17][21]. As such, the real problem in seawater electrolysis is not to produce hydrogen, but to maintain efficient and selective operation under chemically harsh and dynamic conditions [12][17]. These electrochemical aspects explain why real seawater should not be considered as a substitute for freshwater for hydrogen production studies [10][21].

A realistic description of solar-driven seawater electrolysis must consider the specific effects of ion-differentiated reactions, competitive anodic reactions, scaling and fouling, and long-term electrode degradation, in realistic conditions [12][21] and so it is critical to know that real seawater composition is necessary to design catalysts, photoelectrodes, and integrated systems that are not only active but also selective, durable and scalable in hydrogen production [15][21][25].

## 2.3 Hydrogen, Oxygen, and Chlorine Evolution Mechanisms in Seawater

In seawater electrolysis, the main desired reactions are the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode, and the major undesired competing reaction is chlorine oxidation which may evolve with chlorine or may form hypochlorite depending on operations. Photoelectrochemical (PEC) seawater splitting is a solar-driven process in which semiconductor photoelectrodes absorb light, generating charge carriers which drive the evolution of hydrogen and oxygen. In comparison to photocatalytic systems, PEC platforms provide better control over charge separation and interfacial reactions, which can improve reaction efficiency and mechanistic tuning [15][17]. This makes PEC seawater splitting especially enticing for clean solar-to-hydrogen conversion. The HER typically takes the form of a proton or water reduction to produce hydrogen gas, and the OER occurs through a multistep oxidation of hydroxide ions or water molecules to oxygen [3][17]. In seawater, the reaction is more complicated than with freshwater electrolysis. Here the environment for the reaction depends greatly on chloride ions and other dissolved compounds. The surface chemistry of catalysts changes greatly. This alters their electrochemical selectivity and the surrounding environment completely. Hydrogen evolution at the cathode is relatively easier than anodic oxidation at most, since chloride ions do not engage in competition with HER as they do with OER in alkaline seawater systems. HER is a general process of the dissociation of water followed by hydrogen adsorption and desorption, and efficiency is highly dependent on catalyst composition, local pH, and interfacial charge transfer kinetics [12]. Although the overall cathodic performance may be mitigated indirectly by the seawater content through scaling, fouling, and local changes in ionic strength, which can reduce the effective active area for sustained operation [21]. But the application of PEC in seawater is still extremely difficult, as the photoelectrodes must operate under light irradiation, electrochemical bias, along with conditions of corrosive saline [12][16]. Competing anodic reactions of chloride ions may have positive effects and

dissolved salts and impurities can lead to fast degradation at the surface, recombination loss and unstable behavior in the long run [12][21].

Thus, large initial photocurrent is not enough for a determination of PEC performance in seawater. Recently, surface engineering, heterojunction system development, cocatalyst loading, and defect regulation have promoted PEC seawater splitting for improving charge separation, selective oxygen utilization, and durability [16][17][23]. Nevertheless, the primary restriction is the equilibrium of activity and stability in realistic seawater [12][23]. Thereby, PEC seawater splitting is a promising scientific approach, but its deployment in applied context would need to be accomplished with more selective, corrosion-resistant, and durable photoelectrode systems. Thus, although HER is easier to stabilize than OER in seawater systems, long-term stability of cathodes is very important [12]. On the anodic side, the evolution of oxygen in seawater is harder because it has to compete with chloride oxidation [12]. The OER is a four-electron process with slow kinetics and therefore requires a large overpotential, especially in the case of non-noble catalysts [12]. In alkaline conditions and OER is more thermodynamically favorable than chlorine evolution and hence alkaline seawater electrolysis is commonly used [12]. Nevertheless, this thermodynamic advantage does not eradicate the problem because chloride-related oxidation can still occur when the catalyst surface is not sufficiently selective, when the overpotential is too high, or when local reaction conditions change over a long period of time [12]. So the practical challenge is not only to accelerate OER, but also to ensure that it does not lead to competing chlorine or hypochlorite pathways [12].

The chloride-related reaction depends highly on pH and anodic potential [12]. In acidic or near-neutral electrolytes, direct chlorine evolution is more likely, while in alkaline electrolytes, chloride oxidation tends to proceed toward hypochlorite-related species [12][24]. Although these side products are avoided in principle, their formation is a considerable problem for the long term because they are lower Faradaic efficiency for oxygen production and lead to electrode degradation and create safety and corrosion problems [23][24]. This is why catalyst selectivity is as important as catalytic activity in seawater electrolysis, especially in solar-driven systems that aim for long-lived and stable hydrogen production [12][23]. The competition between OER and chlorine-related oxidation is also a function of catalyst surface chemistry [12][16]. If anodic materials are fast to charge transfer and the surface of the anodic material is reconstructed under the operating conditions (when the cell is unstable or highly reactive), the chances of parasitic chloride oxidation and catalytic dissolution are also increased [12][23]. In this sense, seawater electrolysis is a trade-off between activity, selectivity, and durability, rather than a simple requirement for high current density alone [12]. Recent research has found that surface engineering, heterojunction formation, cocatalyst decoration, and defect design are useful to improve charge separation and oxygen selectivity but are still needed in real seawater and not just when performing at laboratory electrolytes [16][17][23]. For a practical analysis of the HER, OER, and chlorine-related mechanisms in seawater, understanding the processes is very important to interpret performance data correctly. A catalyst with high initial photocurrent (current density) and high initial temperature is not necessarily suitable for real seawater hydrogen production if it is also subject to chloride corrosion, low oxygen selectivity, or fast degradation [12][24]. A mechanistic understanding in seawater electrolysis and long-term stability and selectivity evaluation are required in order to identify viable solar-driven seawater electrolysis systems [15][21][25].

### 3. Results and Discussions

#### 3.1 key performance metrics for seawater electrolysis

Evaluating seawater electrolysis systems is not only based on hydrogen production. An electrochemical, photoelectrochemical, stability, selectivity, and techno-economic analysis is needed in order to assess the safety and feasibility of the systems to scientifically determine if a system is scientifically promising and scalable [13][17][21]. In solar-driven seawater electrolysis, one cannot only base a system on the high initial current or photocurrent performance, but also on oxygen selectivity, resistance to chloride corrosion, catalyst health and overall performance of the system under realistic operating conditions [12][21][24].

Therefore, a comprehensive performance framework must be established for comparing different seawater electrolysis pathways equally and to identify which one is better for a long-term hydrogen production system [15][21][25]. Electrochemical, the most frequently reported metrics are current density, overpotential, Tafel slope and onset potential [12][23][24] and so on. The current density indicates the rate of hydrogen or oxygen production per electrode area, which is particularly significant when it comes to the industrial activity as the system is expected to be in high current density for long times [23]. Overpotential is the extra energy needed beyond the thermodynamic potential to drive the reaction, while the Tafel slope is used to assess the reaction kinetics and compare the catalytic efficiency between materials [12][23]. For seawater systems the latter are particularly important since a low overpotential, and good kinetics are needed to prevent competition of chlorine-related reactions and to improve anodic selectivity to oxygen evolution [12][23][24]. For photoelectrochemical and photocatalytic systems additional light conversion parameters like solar to hydrogen

efficiency (STH), applied bias photon-to-current efficiency (ABPE), and incident photon-to-current efficiency (IPCE) are needed. These measures indicate how efficiently absorbed light is converted to electrochemical charge and then hydrogen [13][17][19]. STH is the most important system metric as it connects the photocurrent generation to actual fuel production efficiency, while ABPE is helpful when external bias is applied and IPCE enables a measurement of wavelength-dependent photoresponse [13][19].

In seawater-based PEC systems, these metrics should always be taken into account and balanced with stability and selectivity as high light conversion efficiency alone does not guarantee the degradation of chloride or long-term reliability which is more important to operating processes [17][21]. Another important group of metrics are selectivity and stability [12][21][24]. Since seawater is composed of chloride ions, the ability of an anode to maintain oxygen evolution over chlorine or hypochlorite is vital for safety and to process efficiency in water electrolysis [12][23][24]. For this reason, Faradaic efficiency, oxygen selectivity and hypochlorite suppression behavior are very relevant in direct seawater electrolysis studies [23][24]. Durability, as well as long-term chronoamperometric or chronopotentiometric stability as well, is essential because a catalyst that only works a short time has little practical value in terms of performance [21][24].

In seawater systems, durability data are more important than in freshwater ones because long-term exposure to salts, impurities and interfacial conditions can lead to corrosion, poisoning, scaling and catalyst dissolution [21][24]. At the system level, mass-transfer and operational details also need to be taken into account in connection with a seawater to hydrogen system (aquatics or photothermal or photothermal-photocatalytic systems) especially for indirect or integrated seawater-to-hydrogen systems. In a vapor-assisted or photothermal-photocatalytic system, hydrogen evolution rate and conversion efficiency are determined by temperature, vapor pressure, vapor generation rate and light production (and the energy intensity of the light) and these parameters are critical to understand what happens in a real reactor to produce hydrogen [14] and in the real world. In fact, seawater electrolysis needs to be evaluated beyond the electrodes and evaluate reactor and transport-related factors as well [14].

Finally, for industrial application technologies such as levelized cost of hydrogen (LCOH), net present cost (NPC), and annual hydrogen production [20] should be incorporated if possible [21][25]. Such metrics are extremely important for hybrid solar energy systems as they provide information on the potential of developing membranes and reactor concepts in connection with the integration of renewable power systems, capital investment and long-term operations cost. To this end, seawater electrolysis systems should not only be assessed on electrochemical or photoelectrochemical performance but also whether they can produce hydrogen at a competitive price at a tolerable cost and low complexity of systems [21][25]. Therefore, the most interesting studies are those that integrate material performance, system stability, and techno-economic feasibility in one assessment.

Table 1 Comparison Between Solar-Driven Seawater Electrolysis and Freshwater Electrolysis

Aspect	Solar-Driven Seawater Electrolysis	Freshwater Electrolysis
<b>Feedstock availability</b>	Uses abundant seawater, which is widely available and attractive for coastal and water-scarce regions [15][21][24]	Depends on purified or deionized water, which may increase stress on limited freshwater resources [15][21][24]
<b>Electrolyte complexity</b>	Chemically complex due to $\text{Cl}^-$ , $\text{Na}^+$ , $\text{Mg}^{2+}$ , $\text{Ca}^{2+}$ , $\text{SO}_4^{2-}$ , dissolved organics, and microorganisms, which affect catalyst behavior and system stability [10][12][21]	Much simpler and more controllable because impurities are minimized, allowing clearer electrochemical behavior and more stable operation [12][21]
<b>Main anodic challenge</b>	Oxygen evolution must compete with chlorine evolution or hypochlorite formation, especially if the catalyst is not sufficiently selective [12][23][24]	OER proceeds without chloride-related competition, making anodic selectivity easier to maintain [12][24]
<b>Corrosion risk</b>	High, especially at the anode, due to chloride-induced corrosion, catalyst degradation, and surface instability [12][23][24]	Lower corrosion risk because aggressive chloride ions are absent [12][24]
<b>Scaling and fouling</b>	More severe because seawater contains $\text{Mg}^{2+}$ , $\text{Ca}^{2+}$ , suspended species, and biological matter that may cause scaling and fouling [21][22]	Lower tendency for fouling and scaling when purified water is used [21]

<b>Catalyst requirements</b>	Requires catalysts and photoelectrodes with high activity, oxygen selectivity, chloride resistance, and long-term durability [12][16][23]	Catalyst design mainly focuses on activity, efficiency, and general stability, with fewer ion-specific constraints [12][16]
<b>System complexity</b>	May require additional strategies such as alkaline adjustment, anti-corrosion design, selective anodes, vapor-phase separation, or pretreatment [21][24][25]	Generally simpler because the feed is cleaner and electrochemical side reactions are easier to control [21][25]
<b>Photocatalytic/PEC stability</b>	More difficult to maintain due to salt effects, parasitic reactions, and surface degradation under illumination [17][21][23]	More stable under controlled laboratory conditions, allowing better reproducibility and longer lasting photoelectrode performance [17][21]

## 4.0 SOLAR-DRIVEN SEAWATER ELECTROLYSIS TECHNOLOGIES

### 4.1 Photovoltaic-Powered Electrolysis (PV-EC)

Photovoltaic-powered electrolysis (PV-EC) is considered one of the well-established solar technologies for generating hydrogen due to the separation of photovoltaic modules and electrolyzers, both of which can be used in isolation to fine-tune each component alone [6,11]. In such a process, electricity is generated by the solar cells from the solar radiation before flowing to an electrolyzer to create hydrogen and oxygen in the electrolyzer. In comparison to direct photocatalytic and photoelectrochemical systems, PV-EC has more engineering possibilities, easier scale-up, and better compatibility with well-entrenched photovoltaic and electrolysis technology. These benefits render PV-EC especially appealing for deployment in the field, particularly where significant solar resource bases have been developed, and renewable hydrogen infrastructure is at an early stage of development.

In seawater, PV-EC can be also implemented indirectly or directly using seawater electrolysis. In the indirect systems, the seawater is purified or processed into vapor or distilled water and then it enters the electrolyzer, so that the exposure of electrochemical elements to chloride and other pollutants is minimized. In direct systems a feedstock of seawater is adopted more directly and reduces demand for freshwater sources while making resource logistics easier but may lead to serious electrochemical problems related to chloride corrosion, catalyst degradation, and competing anodic reactions. As a consequence, while PV-EC is structurally simpler than fully integrated PEC systems, its effective application with seawater still relies on electrolyte management and electrode endurance. PV-EC's unique features come from its modular design and high flexibility of the system. As the solar harvesting element is decoupled from the electrolysis platform, each sub-system can be further developed independently, rather than having to completely reinvent the system. This decoupled structure opens the door to more sophisticated solar cells, hybrid renewable sources, and traditional electrolyzer schemes being used – key benefits as photocatalytic systems must strike the balance of light absorption, charge separation, and surface catalysis inside the same construction. Accordingly, PV-EC is the most practical short-term means of achieving high solar hydrogen production.

However, application of PV-EC to seawater electrolysis is a complex technology. In the anode, oxygen evolution has to contend with a competitive competition with chloride-related oxidation at the anode, particularly for high overpotentials or inadequate catalyst selectivity. This is an important consideration, given that industrial hydrogen production is operationally limited to a long-term process at high current densities, under which small reductions in selectivity can cause hypochlorite formation, corrosion, and electrode failure to occur relatively soon. So, PV-EC systems for seawater demand highly active and chloride-resistant electrocatalysts whose duration of operation is high enough to enable oxygen-selective function. Recent research has reported substantial success when catalyst design and system construction are complementary in this regard. For instance, seawater electrolysis systems in alkaline media lead to some of the most successful oxygen selectivity since in alkaline media, the thermodynamic favourability of chlorine evolution vis-a-vis oxygen evolution becomes weaker.

Furthermore, corrosion-resistant multilayer anodes and surface-protected catalyst architectures have proven to be capable of conducting high-current seawater electrolysis for long timescales, and it can therefore be realized that direct solar-driven seawater electrolysis can become viable once electrode stability is provided for on a structural level. Such results indicate that the prospects of PV-EC technology from seawater use in future to achieve photovoltaic performance shall be determined partly by their effectiveness as well as catalyst protection, anodic selectivity and materials resilience. Another prominent role of PV-EC is techno-economic optimization. As photovoltaic units and electrolysis entities are discrete, system cost could be more accurately assessed through metrics such as electricity efficiency, annual hydrogen production, net present cost, or levelized cost of hydrogen. Such systems, which can be combined with hybrid renewables such as solar-wind, make PV-EC more conducive to systems integration in a systematic way based on power variation patterns, component configuration needs, and lifetime economics. But for the economic applicability of direct seawater PV-EC, it remains the case that the level of corrosion can be optimized for performance levels, which in operation can then be further minimized through pretreatment demand and maintenance requirements. Overall, PV-EC offers the most technologically advanced and commercially feasible solar-based hydrogen pathway compared to the available seawater

electrolysis. Its modular structure, compatibility with the commercial solar technologies, and high scalability offers significant advantages relative to more integrated photocatalytic or PEC pathways. However, in direct application of real seawater, issues of anode selectivity, degradation due to chloride and long-term stability are unsolved. As a result, in the future, efforts for the development of PV-EC for seawater hydrogen production should target the coupling of high-efficiency solar power generation with powerful, oxygen selective, corrosion resistant electrolysis systems that can achieve a realistic industrial operation.

#### 4.2 Photoelectrochemical (PEC) Seawater Splitting

Photoelectrochemical (PEC) seawater splitting is a solar-based process where semiconductor photoelectrodes absorb light and generate charge carriers that propel hydrogen and oxygen evolution reactions [3][15][17]. Compared with photocatalytic systems, PEC platforms have superior control over charge separation and interfacial reactions which can enhance reaction efficiency and mechanistic tuning [15][17]. This also makes PEC seawater splitting an appealing platform for direct solar-to-hydrogen conversion. Nevertheless, it is still very difficult to perform PEC in seawater as it is necessary to be operated under simultaneous light irradiation, electrochemical bias, and corrosive saline conditions with photoelectrodes [12][16].

Chloride ions may induce competing anodic reactions and dissolved salts and impurities may stimulate surface damage, recombination loss, and long-term instability [12][21]. Thus, the high initial photocurrent per se is not adequate to evaluate the PEC performance in seawater. The surface engineering, heterojunction construction, cocatalyst loading and defect regulation recently identified PEC seawater splitting technologies to improve charge separation, oxygen selectivity, and durability [16][17][23]. Nonetheless, the only major constraint is the trade-off between activity and stability with natural seawater conditions [12][23]. Thus the technology of PEC seawater splitting system is scientifically promising, but there is still a need for the development of a technology that is more selective, corrosion-resistant and long-lasting for practical application of PEC seawater splitting systems..

#### 4.3 Vapor-Phase Solar Water Splitting

Vapor-phase solar water splitting is an indirect route that converts seawater to water vapor and this vapor is then used for hydrogen production [15] and is attractive because it has no direct contact between the liquid seawater and catalyst surface and thus less chloride corrosion, salt accumulation, and fouling which are common and may cause problems with direct seawater electrolysis [21]. So vapor-phase systems are a natural way to separate the seawater management from the hydrogen generation process. Most designs combine photothermal vapor generation with photocatalytic or photo-assisted water splitting with solar energy to support both evaporation and hydrogen production [15]. This combined design has the potential to enhance operational safety and catalyst protection especially in saline applications [21].

However, the overall performance is still limited by low vapor-splitting efficiency, heat losses, and the difficulty of optimizing vapor transport, light absorption and catalytic conversion simultaneously [6][21]. Therefore, vapor-phase solar water splitting is promising for seawater-to-hydrogen systems because it can alleviate several corrosive effects of real seawater, but its large-scale application still depends on improved photothermal materials, more efficient vapor-fed catalysts, and better system integration [15][21].

### 5.0 ADVANCED CATALYSTS FOR SEAWATER ELECTROLYSIS

The development of high-performance catalysts is critical to seawater electrolysis as catalyst performance is critical not only in reaction activity, but also in corrosion resistance and long term stability under saline conditions [12][15]. Unlike freshwater systems, seawater electrolysis requires catalysts to ensure efficient hydrogen and oxygen evolution in the presence of chloride ions, dissolved salts as well as other impurities which may lead to parasitic reactions or structural degradation [12]. Therefore, catalyst design for seawater electrolysis needs to consider more than simply improving activity.

In the cathodic domain, the catalysts are mainly developed to accelerate hydrogen evolution reaction, decreasing charge transfer resistance and facilitating water dissociation, especially in alkaline media [12]. On the anodic side, the problem is more complicated as oxygen evolution should proceed selectively. As a result, anode catalyst design has emerged as the main focus of seawater electrolysis research for solar-driven systems where high activity is required to balance long-lasting structural stability [12][15]. The most recent catalyst designs include transition metal-based electrocatalysts, defect-engineered materials, heterojunction structures, cocatalyst decoration and surface-regulated photoelectrodes, and so on for better separation of charges, higher active site density, lower overpotential and stability of catalytic surfaces during long-term operation [16][17][23]. However, more active catalyst work does not necessarily mean better durability.

Most of the time, highly active catalysts are also at risk of dissolution, reconstruction or chloride attack and it is important to stress the fact that in seawater electrolysis there is a trade-off between activity, selectivity and stability

[12][23][24]. Therefore, the most promising advanced catalysts are not those with the highest initial current density but those that are able to maintain selective oxygen and hydrogen evolution with little degradation in realistic seawater conditions [12][21][24]. Therefore, increasingly recent research has considered catalysts using a combination of overpotential, Tafel slope, Faradaic efficiency, hypochlorite suppression and long-term stability, rather than activity data alone [12][23][24]. A broader view of performance is therefore important to identify catalysts that are relevant to practical seawater hydrogen production [15][25].

## 6.0 PERFORMANCE METRICS & MECHANISMS OF CATALYSIS GRAPHENE-BASED ELECTROCATALYSTS

Long-term stability is for the practical applications of solar-driven seawater electrolysis systems a very serious long-range constraint. Seawater is a challenging environment that has a lot of chemical species and a fast-acting interface to catalyst and system failure [12][24]. Therefore, the life span of electrodes and photoelectrodes is also the most important question in terms of general application and economic feasibility of operation performance [12]. Corrosion due to chloride is one of the most significant degradation mechanisms for seawater electrolysis, which in seawater electrolysis would lead to pitting, surface roughening and loss of active material at anodic sites. Chloride ions easily penetrate oxide layers and can damage protective surface films, especially on transition metal catalysts and lead to rapid decay. Also, due to parasitic chlorine evolution reactions, they produce reactive chlorine species, which further enhances corrosion and chemical destabilization of the electrode materials [16][24].

Scaling/surface fouling is another major degradation factor, especially at cathodic sites. Multivalent cations  $Mg^{2+}$  and  $Ca^{2+}$  precipitate in local alkaline conditions as hydroxides or carbonates in an insulating layer that impairs active sites and increases interfacial resistance [12][24]. Besides the negative effects of these compounds on catalytic processes they also interfere with mass transport and gas release and lead to high overpotentials and unstable operation (and hence long term stability) in long-term operations [12]. Finally there can be further fouling due to dissolved organic matter and biological organisms in the natural seawater [10] for photocatalytic and photoelectrochemical systems, and for such systems it is also not only harmful for the long term stability. Photo corrosion is a critical problem for photo-assisted seawater electrolysis in oxide or sulfide photoelectrodes [3][14]. Photogenerated holes can oxidize the semiconductor in a photo-assisted seawater electrolysis system (and not water molecules) and lead to irreversible structure degradation and the loss of photoactivity with an irreversible deterioration and rapid loss of photoactivity under light and the degradation of the semiconductor when the semiconductor is illuminated and photoactivity with a light is at its low level and in the presence of chloride ions the surface states begin to destabilize and then become unstable and can produce unwanted side reactions [12][19]. These problems make it essential to have corrosion resistant photoelectrode based on photo-assisted electrolysis with oxide or sulfide photoelectrodes to perform well in seawater electrolysis systems, and therefore it is necessary to have corrosion-resistant photoelectrode designs that are suitable for taking the lead in this process in seawater electrolysis, which can be used for conducting photoelectrode electrolysis.

In the last few years, various stability enhancement techniques have been developed on how to reduce the degradation process. Surface engineering techniques can be used to reduce the penetration of chloride on catalysts and stabilize the catalyst surface, but not to the detriment of the catalyst performance [16]. The self-reconstructive surface nanostructured catalysts with self-reconstructed materials can also be developed to allow for stable hydroxide layer development and provide partial anti-corrosion when catalysts are used [12]. The vapor-phase solar water splitting system reduces the contact of catalysts with liquid seawater, which minimizes corrosion, scaling and fouling and significantly improves durability [21][24] despite better performance than other liquid-phase systems. However, long term behaviors in >3k h in actual seawater situations in the long term are always the important issue. Some systems clearly work well in the short term but with great degradation later than the time in lab [12][24]. Thus, long term durability testing with realistic seawater compositions in a long term range is the most important to study the performance of the system and to point out future material et al. design and construction.

### 6.1 Major Degradation Mechanisms and Mitigation Strategies in Solar-driven Seawater Electrolysis

Current mitigation strategies for alkaline operations, surface engineering, protective coatings, heterojunction design, cocatalyst decoration, and multilayer corrosion-resistant electrodes are all currently available [12][16][23][24]. Alkaline conditions are preferred because they provide better oxygen evolution selectivity, as compared to chlorine-induced oxidation [12][24]. Surface-controlled catalysts and coated anodes can also reduce direct chloride attack and improve durability, while heterojunctions and conductive supports can help to control charge transport and prevent recombination in solar-driven systems [16][17][23]. But no single approach has solved the challenges of corrosion resistance, selectivity and long-term stability in seawater [21][24]. So, the future research should focus on the combination of material protection, selective catalysis, and realistic long-duration testing to identify systems that are active and stable in the real world [15][25].

Table 2 Comparison of Degredation Mechanism, Primary Cause and Impact on Performance

Degradation Mechanism	Primary Cause in Seawater	Impact on Performance
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Chloride-induced corrosion	Aggressive Cl <sup>-</sup> attack on catalyst or electrode surface, especially at the anode [12][24]	Surface degradation, loss of active material, reduced durability, lower oxygen selectivity
Chlorine / hypochlorite side reaction	Insufficiently selective OER catalyst, high overpotential, unstable anodic surface [12][23][24]	Lower Faradaic efficiency for oxygen evolution, safety concerns, faster electrode degradation
Catalyst dissolution / surface reconstruction	Highly reactive active phases, prolonged anodic polarization, unstable high-valent metal states [12][23]	Loss of catalytic sites, performance decay, activity–stability trade-off
Scaling / salt precipitation	Deposition of Mg <sup>2+</sup> , Ca <sup>2+</sup> , and other dissolved species under alkaline or concentrated conditions [12][21]	Blocked active sites, reduced electrode area, slower charge transfer
Surface fouling / poisoning	Dissolved organics, suspended solids, biological impurities, or adsorbed species from real seawater [21][22]	Reduced catalytic accessibility, unstable long-term performance, lower reproducibility
Photo corrosion	Light-induced degradation of photocatalyst or photoelectrode under saline conditions [17][21]	Reduced photo response, material instability, shortened operating lifetime
Charge recombination increase	Poor charge separation, defect accumulation, interfacial instability in photoactive materials [16][17]	Lower photocurrent, reduced efficiency, weaker hydrogen production

## 7.0 ENVIRONMENTAL AND ECONOMIC CONSIDERATIONS

The environmental sustainability and economic sustainability of solar-driven seawater electrolysis in terms of solar-driven seawater electrolysis are important to determine its feasibility to produce large quantities of hydrogen. Seawater is a plentiful and readily available source for production of hydrogen, but its direct use creates environmental and cost-related issues that require further study [2][6]. Seawater electrolysis systems make less use of freshwater which is a more efficient choice than conventional freshwater electrolysis and is much more sustainable on both material and system level [24]. Control of parasitic chlorine evolution reactions is also important to prevent the release of chlorine-laden species that could affect the environment and lead to environmental degradation in marine environments [12]. In poor conditions seawater electrolysis can release chlorine gas or hypochlorite which may harm the environment [16]. Additionally, when catalysts and electrodes are degraded, metal ions and particulate matter can be released into the seawater, and the environmental degradation potential in the long run is high [24].

For seawater electrolysis applications selective catalysis, containment strategies, and environmentally friendly design of systems are important factors [12][23]. However, the economical aspects are closely related to sustainability of long life, material and power use of a system. PV-based electrolysis systems have low cost of solar modules, while the cost of corrosion-resistant catalyst systems, coatings and seawater-tolerant reactor parts may lead to a higher CAPEX; the cost of corrosion-resistant catalyst [2][25]. Also, the operational expenditure (catalyst lifetime, maintenance and system downtime due to scaling and fouling) affects the computational cost of the electrolysis. So, it is not just about efficiency metrics, but also sustainability and the sustainability of the system in practice [6]. So integrated systems can provide the added benefit of environmental and economic results. Hybrid PV-wind-based seawater electrolysis systems could help to achieve energy efficiency and reduce intermittency losses and thus the overall efficiency of hydrogen production [25].

The same can be said of the integration of hydrogen production with other processes such as pollution removal or desalination to contribute to the environment as well as operating costs [20][23]. These systems are complex and need to be optimized for system reliability and scalability [24]. With this, while there are significant steps up the way, the environmental and economic attractiveness of solar-based seawater electrolysis remains to be determined by catalyst durability, system integration and long-term operational stability. Life cycle and techno-economic analysis for realistic seawater scenarios are of utmost importance for directing the research and development pathway towards sustainable and economical hydrogen production [6][25].

## 8.0 FUTURE PERSPECTIVES

Therefore, considering this development, building synergistic materials design, systems design and operation in saline environments will be a crucial area for further advancements in solar led seawater electrolysis. While several studies exhibited effective performance in the lab, generalization of these achievements to longer term scalable systems is still complicated by the chemistry of real seawater [12][24]. These issues require a paradigm shift from the fast optimization of catalyst activity on the fly to a comprehensive study of stability, selectivity, and long-term operational behaviour in a realistic scenario, and it should be incorporated into more advanced technologies.

Electrocatalysts and photoelectrodes in seawater are also of interest from a material point of view. Facets for instance, that will later be catalysts, will be determined to be selective at both an oxygen evolution and surface interface by preventing chloride adsorption and parasitic reactions. Defect modulation, heterostructure formation and surface reconstruction with controlled properties may be possible to enhance the durability with little impact on catalysis [12][16]. Corrosion resistant semiconductor materials, such as doped oxides and III-V nanostructures for photo assisted systems (e.g., in chloride environments) can reduce photo corrosion and enhance the stability of photoelectrode by long-term electrochemical growth [4][19]. Moreover, the system-wise design optimization will be even more significant to be able to improve performance and durability. The vapor-phase separation of catalytic reactions from seawater is therefore an interesting way to do this and may help reduce erosion, scaling and fouling [21][24].

The hybrid system with photovoltaic, wind or solar energy is also found to be more efficient and less stressful to electrolysis components [6][24]. But the thermal and electrical management of such facilities is key to maintaining stable system operation and economic feasibility [24]. Another important future focus is to standardize the experimental protocols for seawater electrolysis. All studies reported so far are based on simulated seawater or short duration experiments and do not reflect the long-lasting degradation behavior of natural seawater [12][24]. However, we expect that the prolonged durability testing with real seawater and the use of in situ or operando characterization-based techniques will help to determine the mode of dominant failure and rational material and system refinements [12].

Lastly, environmental and techno-economic studies will be conducted to determine the feasibility of large-scale application. Therefore, future studies should incorporate life-cycle effects, catalyst lifetime, maintenance needs and system infrastructure costs so that realistic estimates of hydrogen production from seawater can be made [2][6][25]. The solar-driven seawater electrolysis will lead to sustainable hydrogen production pathways, addressing specific interdisciplinary challenges and developing seawater-related design solutions to make it practical [23][24].

## 9.0 CONCLUSION

Sun-assisted seawater electrolysis is a new approach to sustainable hydrogen generation and a promising method to reduce water emissions through solar systems that can be used to generate significant quantities of hydrogen from a rich and renewable source (seawater). This system has great advantages in comparison to the existing electrolysis from freshwater sources, particularly in terms of regional flexibility, especially in coastal and offshore seawater applications. However, direct seawater electrolysis is also associated with a lot of electrochemical problems, from chloride corrosion effects to competing chlorine evolution reactions, scaling from multivalent cations, and less long-term stability, which would restrict practical use [12][24].

In this review, the chemistry of seawater electrolysis and the main performance characteristics were determined, and the major solar-based systems such as photovoltaic-based electrolysis, photoelectrochemical systems, photocatalytic systems, and vapor phase water splitting were defined. Both these systems are known to have advantages and disadvantages, and no different system will adequately fulfil the requirements of efficient, robust, and scalable solutions in practical seawater systems [6][21]. Recent advances in catalyst design, surface engineering and new methods of photoelectrode creation have yielded significant advances in this domain – mainly in the areas of additional improvement of oxygen evolution and reduction of chloride-related deterioration [12][16]. Even as advances were made, long-term stability remains an issue.

A number of these reported systems exhibit good short-term performance but degrade over an extended period in conditions of natural seawater. Successful implementation will lead the scientific community to more holistic, realistic testing conditions, and seawater-specific advances, as emphasized in this review [12][24], rather than the performance of isolated systems. For this purpose, vapor-phase approaches and hybrid renewable energy embedding are feasible alternatives to liquid-phase seawater electrolysis [21]. Solar seawater electrolysis as a potential green hydrogen infrastructure in the future is, on the whole, a major hope. Now, it is with a coordinated strategy between materials science, electrochemical engineering, and system-level architectures using standardized test protocols and detailed techno-environmental studies that we will make progress. Challenges of this nature need to be confronted in seawater research and development if this technology is to take a much closer step toward having the potential for mass production of hydrogen and for transitioning to clean energy in the global economy [24].

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