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Toward Practical Seawater Splitting: Challenges, Recent Breakthroughs, and Prospects for Scalable Hydrogen Production

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ABSTRACT

Seawater electrolysis has emerged as a compelling pathway for green hydrogen production, enabling the use of Earth's most abundant water resource while preserving limited freshwater reserves. However, direct seawater splitting remains fundamentally more complex than conventional electrolysis in purified media due to chloride-induced corrosion, chlorine evolution, inorganic scaling, and membrane and catalyst degradation in a multicomponent electrolyte. Recent advances in electrocatalyst design and system engineering are beginning to close this gap. Strategies such as chloride-tolerant and self-protective OER catalysts, layered double hydroxides with tailored anion intercalation, single-atom and noble-metal-modified active sites, and nanostructured HER catalysts with anti-fouling architectures have significantly improved activity, selectivity, and durability in saline environments. In parallel, system-level innovations including anion-exchange and asymmetric membrane configurations, multi-chamber and buffered-cell architectures, hybrid anodic reactions that bypass oxygen evolution and suppress chlorine formation, and integrated pre-treatment and flow management have enabled stable, chlorine-suppressed operation in real or simulated seawater for thousands of hours at practically relevant current densities in a limited number of prototype systems. This review consolidates the rationale for seawater splitting, compares indirect (desalination-coupled) and direct approaches, analyzes key degradation and selectivity challenges, and highlights recent breakthroughs in materials and reactor design that are pushing seawater electrolysis toward technological viability. Finally, the broader environmental and infrastructural implications are discussed, underscoring seawater electrolysis as a promising route to scalable green hydrogen that decouples clean energy deployment from freshwater consumption.

Introduction

Hydrogen is widely regarded as a pivotal clean energy carrier for the global transition away from fossil fuels. When used as fuel, hydrogen generates only water vapor with zero greenhouse gas emissions, offering high energy density and versatility for decarbonizing hard-to-abate sectors [1]. Traditionally, most hydrogen is produced from fossil resources, incurring significant carbon emissions and other environmental costs [1].

In contrast, water electrolysis powered by renewable electricity can yield "green hydrogen" with no direct emissions [1]. Scaling up electrolysis to meet future hydrogen demand, however, raises concerns about water consumption. Producing 1 kg of hydrogen via water splitting theoretically requires about 9 L of water, and additional volumes may be needed for purification and cooling in practical systems [2].

If a substantial share of future hydrogen production relies on freshwater, the impact on local water supplies could become critical, particularly in arid and water-stressed regions or where hydrogen plants are co-located with other major water users [2, 3].

Seawater presents an attractive solution as an electrolysis feedstock. Covering ~71% of the

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planet's surface, oceans represent nearly inexhaustible reserves of water [3]. Over 96% of Earth's water is saline, making seawater an abundant and widely available electrolyte for hydrogen generation [1]. By tapping into seawater, hydrogen can be produced without depleting freshwater resources, preserving potable water for human and agricultural needs (Figure 1) [3]. This is especially important because freshwater is unevenly distributed and already scarce in many areas where renewable energy potential is high [3]. Efficient seawater electrolysis would alleviate pressure on lakes and aquifers while providing a continuous clean energy supply from the oceans. Moreover, integrating seawater electrolyzes with offshore renewable power (such as wind turbines or floating solar panels) could enable on-site hydrogen production at sea. The hydrogen produced can fuel ships, marine platforms, and coastal industries directly, fostering a marine energy economy with minimal carbon footprint [3].

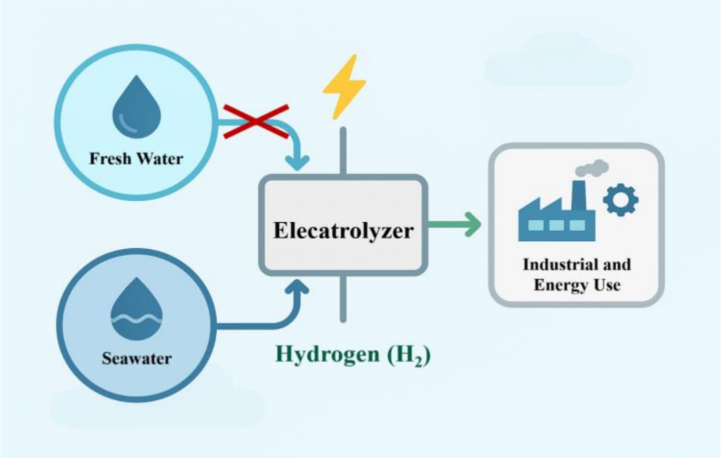

Figure 1. Schematic illustration of hydrogen production using seawater as the feedstock for electrolysis. By utilizing seawater instead of freshwater, the process produces hydrogen without depleting potable water resources, supporting sustainable energy generation for industrial and energy applications.

Despite its promise, seawater electrolysis faces several formidable challenges that hinder its practical implementation. A major obstacle is the anodic oxidation of chloride ions (Cl^-) to chlorine gas (Cl_2) or hypochlorite (ClO^-), which competes with the desired oxygen evolution reaction (OER). These chlorine-related reactions not only lower the faradaic efficiency for hydrogen production but also generate corrosive and toxic by-products that degrade system components. Additionally, the complex ionic composition of seawater (including Mg^{2+}, Ca^{2+}, and SO_4^{2-}) can cause electrode fouling and catalyst poisoning through the formation of insoluble precipitates such as $Mg(OH)_2$, which block active sites and impede reaction kinetics. Catalyst degradation is further exacerbated by interactions with dissolved organic matter, microorganisms, and fluctuating pH levels during operation. Moreover, electrode corrosion, particularly at the anode, remains a persistent issue due to the aggressive nature of Cl^- ions under oxidative potentials, significantly limiting the durability and lifespan of conventional materials. The neutral to slightly alkaline pH of seawater also results in sluggish HER and OER kinetics, thereby increasing the overall energy consumption of the system. To address these multifactorial barriers, recent research has focused on the development of selective and corrosion-resistant electro catalysts that can suppress chloride oxidation while maintaining high activity for HER and OER. Key strategies include applying protective coatings to electrode surfaces to prevent fouling and chloride ingress, and optimizing electrolyzer architectures to enhance bubble release and reduce ion crossover. Additionally, introducing electrolyte additives can inhibit chlorine evolution or stabilize catalyst surfaces. Together, these material and engineering innovations are crucial for enabling robust, long-term seawater electrolysis under realistic operating conditions [4-14].

As illustrated in Figure 2, seawater splitting offers several major advantages, including resource abundance, decoupling hydrogen production from freshwater consumption, and the potential for sustainable large-scale implementation, particularly in coastal and arid regions where seawater is readily available.

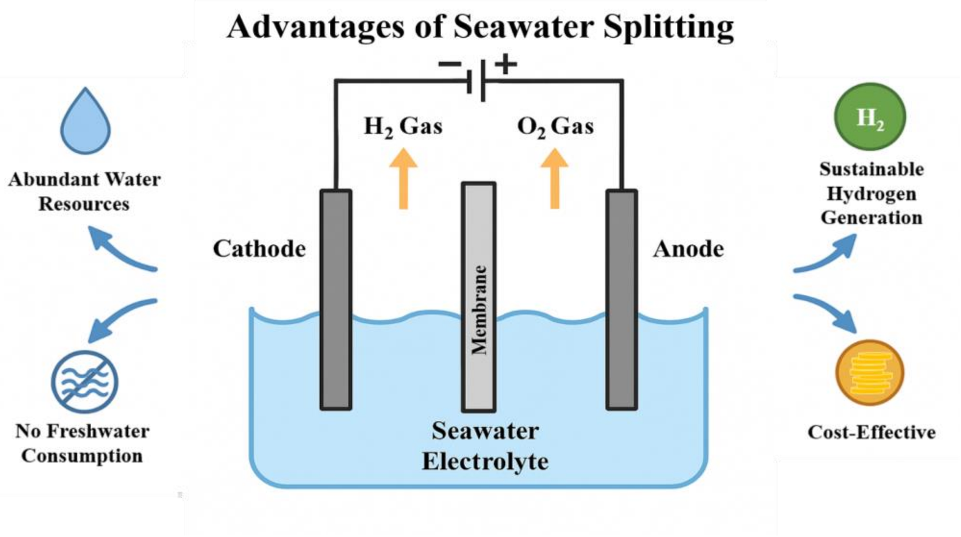

Figure 2. Schematic illustration highlighting the key advantages of seawater splitting for hydrogen production.

This process utilizes abundant oceanic water resources, thereby minimizing reliance on freshwater supplies. It offers a sustainable pathway for large-scale hydrogen generation while potentially reducing water supply constraints and simplifying logistics in suitable coastal and offshore settings, making it an attractive option for future low-carbon energy systems.

Although promising, direct seawater electrolysis is far more challenging than conventional water splitting using purified water. Seawater is a complex mixture of dissolved salts, primarily sodium chloride, along with significant amounts of other salts containing Mg^{2+}, Ca^{2+}, and K^{+} ions, as well as organic matter and microorganisms [3]. These components can interfere with the electrolysis reactions and damage the electrodes. Two issues are especially problematic. First, the ubiquity of chloride ions (Cl^{-} ~0.5 M in seawater) leads to competitive electrochemical reactions that divert efficiency and create hazardous by-products [1, 3]. Instead of the desired oxygen evolution reaction (OER) at the anode, chloride can be oxidized to chlorine gas or hypochlorite (the chlorine evolution reaction, CER) at lower potentials [1]. Chlorine generation not only wastes energy but also causes serious corrosion of equipment and poses toxicity risks [3]. Second, the presence of chloride and other ions accelerates the degradation of most conventional electrode materials. Chloride-induced corrosion and catalyst dissolution drastically shorten the lifetime of electrodes in seawater conditions [1]. Additional challenges include electrode fouling caused by precipitated salts (e.g., $Mg(OH)_2$ and $CaCO_3$) that form through reactions with hydroxide ions generated during hydrogen evolution. Moreover, the complex buffering and speciation of seawater (e.g., the carbonate system) can hinder local pH control and reaction selectivity, despite its inherently high conductivity [3]. Overcoming these hurdles requires a multifaceted approach spanning materials science, catalysis, and engineering design [15]. In the following sections, we discuss the rationale for seawater splitting in greater detail, survey current technological approaches, examine the key technical challenges, and review recent progress in electro catalysts and system designs that are pushing seawater electrolysis toward practical reality.

Rationale for Seawater Splitting

The primary driver for seawater splitting is the need to scale up green hydrogen production without straining global freshwater reserves. Freshwater is a limited resource essential for human consumption, agriculture, and ecosystems; large-scale, localized diversion of clean water for hydrogen production could exacerbate water stress and competition among sectors, particularly in arid and semi-arid regions [3]. By contrast, seawater is essentially limitless and underutilized for energy production. Utilizing seawater as the electrolyzer feed offers a sustainable pathway to hydrogen that decouples energy and freshwater resources [3]. This is particularly relevant for Sun Belt regions and small island nations with abundant solar/wind potential but limited freshwater. Directly electrolyzing seawater could enable hydrogen fuel production in these areas without importing water, thereby accelerating renewable energy adoption and energy independence.

In addition to conserving freshwater, seawater electrolysis opens opportunities for in situ hydrogen generation in marine environments. Offshore wind farms, for example, could be coupled with seawater electrolyzes to produce hydrogen on-site, converting intermittent electricity into a transportable fuel [3]. The hydrogen could then be shipped or piped to shore, or even used at sea for powering ships and marine equipment [3]. This integration of offshore renewables with seawater electrolysis can create a novel clean energy system wherein the ocean serves both as the energy source (via wind/waves/solar) and the reaction medium for hydrogen production. Such systems would reduce the need for undersea transmission cables by locally converting electricity to hydrogen. Furthermore, hydrogen production platforms at sea could supply fuel for maritime industries, reducing reliance on fossil fuels for shipping and port operations [3]. The co-location of energy harvesting and fuel production offshore exemplifies the environmental synergy enabled by seawater splitting leveraging ocean resources to generate zero-carbon fuel while preserving terrestrial resources.

Beyond energy considerations, seawater electrolysis has potential ancillary benefits. The electrolysis process inherently produces oxygen (at the anode) along with hydrogen; in seawater this oxygen could potentially be vented to oxygenate local waters or captured for industrial use, although such applications remain largely conceptual and require further evaluation. Additionally, certain electrolysis designs may allow recovery of valuable minerals from seawater. For instance, magnesium and calcium ions that precipitate during cathodic hydrogen evolution can be harvested as hydroxides, which have commercial value [3]. Research suggests it is feasible to co-produce magnesium hydroxide at the cathode by controlling local pH around ~9-10, given $Mg(OH)_2$ precipitates at pH ~9.3 [3]. Although still conceptual, this hints that future seawater electrolyzes might function as dual-purpose systems for hydrogen fuel and mineral extraction, provided that the associated separation, purity, and economic constraints can be met. In summary, the rationale for seawater splitting is compelling: it promises to unlock vast quantities of green hydrogen by tapping an abundant resource, mitigating the water footprint of the hydrogen economy, and enabling new integrated energy systems on and off the shores.

Current Technologies and Approaches

Several technological approaches have been explored to realize seawater electrolysis, each aiming to address the unique challenges posed by saltwater. Broadly, strategies can be classified into direct and indirect seawater electrolysis. In direct approaches, the electrolyzer feeds on raw or minimally treated seawater, and the cell is engineered to cope with impurities and avoid side reactions. In indirect approaches, seawater is first desalted or purified (fully or partially) before entering a conventional water electrolyzer, thereby avoiding many seawater issues at the cost of extra processing.

Conventional Electrolyzes: A baseline for comparison is the standard water electrolyzer technology (alkaline or proton-exchange membrane cells) operating on purified freshwater. These systems, if fed with actual seawater, typically suffer rapid failure from chloride corrosion and electrode poisoning. Therefore, early "seawater" electrolysis implementations physically separated the desalination and electrolysis steps. For example, seawater can be desalinated via reverse osmosis or distillation, then the clean water is fed to a regular electrolyzer [16]. This two-stage approach is effective in eliminating side reactions and corrosion, since the electrolyzer never directly contacts chloride or multivalent ions. Indeed, most commercial hydrogen projects near coastlines currently rely on an upstream desalination unit [16]. However, the need for a dedicated desalination plant adds capital cost and energy consumption, reducing overall efficiency and flexibility [16]. The additional energy required for pre-desalination (typically 3-5 kWh per cubic meter of water) can offset some of the gains of using seawater and makes the hydrogen more expensive [16]. Moreover, the equipment footprint grows, which is problematic for offshore or space-constrained installations. Thus, while indirect seawater splitting is feasible, it is not the ideal solution from an economic and systems perspective [16].

Direct Seawater Electrolysis: The focus of recent research has been on direct seawater electrolysis (DSE), where the cell directly processes seawater in one integrated system. The challenge is to redesign catalysts, membranes, and cell architecture such that the detrimental reactions are suppressed and components withstand the harsh electrolyte [15, 16]. A number of advances have been made in this direction:

- ✓ **Membrane and Electrolyte Engineering:** A straightforward approach is to modify the electrolyte environment seen by the electrodes. Some systems use a buffered or hybrid electrolyte: for example, a concentrated alkaline solution is added to or circulated alongside seawater to maintain favorable pH and suppress chlorine chemistry. Anion-exchange membranes (AEMs) can be used to allow only hydroxide (OH^-) transfer while impeding chloride access to the anode. In one design, a three-compartment electrolyzer with dual AEMs was introduced to isolate the anode from raw seawater [3]. In this configuration, a thin layer of alkaline solution contacts the anode, separated from a middle compartment of seawater by an AEM, while a second AEM separates the seawater compartment from the cathode. This dual-membrane setup effectively creates a protective buffer zone: OH^- ions can migrate to the anode to sustain OER, but chloride is largely confined away from the anode, dramatically reducing chlorine evolution and corrosion [3]. A landmark demonstration of this concept was reported by Xie et al., who operated a membrane-based direct seawater electrolyzer at 250 mA cm^{-2} for over 3,200 hours with negligible degradation [16]. By radically solving the side-reaction and corrosion problems through cell architecture, they achieved seawater splitting performance comparable to conventional water electrolysis without a significant cost penalty [16]. This proof-of-concept indicates that smart cell design (using tailored membranes and electrolyte management) can enable stable long-term hydrogen production from natural seawater.

- ✓ **Hybrid Anode Reactions:** Another approach to direct seawater electrolysis is to avoid the problematic oxygen evolution reaction altogether by using an alternative anodic reaction that is more energetically favorable and does not produce chlorine [1]. In such hybrid seawater electrolyzes, the cathode still performs the hydrogen evolution reaction (HER) on seawater, but the anode performs a different oxidation reaction (using a solute added to the water) instead of OER. For example, one study coupled seawater HER with the oxidation of sulfide (S^{2-}) ions to elemental sulfur at the anode, using a functional Co_3S_4 catalyst [1]. Oxidizing sulfide (which can be sourced from industrial waste or added as Na_2S) requires a much lower potential than OER, thus lowering the cell voltage and completely avoiding chlorine generation since chloride is not oxidized at those potentials. This allowed the system to sustain 100 mA cm^{-2} hydrogen production for over 500 hours with no chlorine by-product. Similarly, other sacrificial or waste-assisted oxidations such as urea oxidation, glycerol oxidation, or even plastic (PET) degradation have been coupled with hydrogen production [1]. These reactions not only sidestep OER and its associated high over potential and Cl_2 issues, but also provide value by treating waste streams or producing useful chemicals. While hybrid approaches require a continuous supply of oxidizable species (e.g., urea or sulfide), they demonstrate an effective concept to lower cell voltage and suppress chlorine formation [1]. However, their large-scale applicability depends on the availability, stability, and management of these feeds and products, and ongoing research is assessing the techno-economic trade-offs between additive consumption and energy savings [1].
- ✓ **Baseline Treatment and Filtration:** Even in direct electrolyzes, some level of pre-treatment is usually employed to remove abrasive solids or biofouling organisms from seawater to protect the cell. Sand filters, micron filters, or ultrafiltration membranes can be used to clear suspended particles and microbes. Additionally, de-aeration of seawater (to remove dissolved O_2/CO_2) can help minimize cathode carbonation or oxidation of sensitive catalysts. These measures, while not eliminating dissolved salt challenges, improve the reliability of seawater-fed cells. Research prototypes often use simulated seawater (a purified salt solution) to have a controlled test medium without organic fouling components [15]. However, demonstrations in real seawater under practical conditions (such as the 3,200 h run mentioned above) are increasing, indicating that with robust design, direct seawater splitting is achievable in the field [16].

In summary, current technologies for seawater splitting range from adding front-end desalination (indirect methods) to advanced integrated electrolyzes that function in raw seawater (direct methods). The state-of-the-art is rapidly evolving, with creative solutions like multi-chamber cells and hybrid anode reactions enabling significant progress. The next sections delve into the core challenges that these technologies must overcome and the innovative electro catalytic materials developed to address them.

Key Challenges in Seawater Electrolysis

The major technical barriers to direct seawater electrolysis include chloride-induced corrosion, side reactions, catalyst instability, and water quality issues, all of which are schematically illustrated in Figure 3.

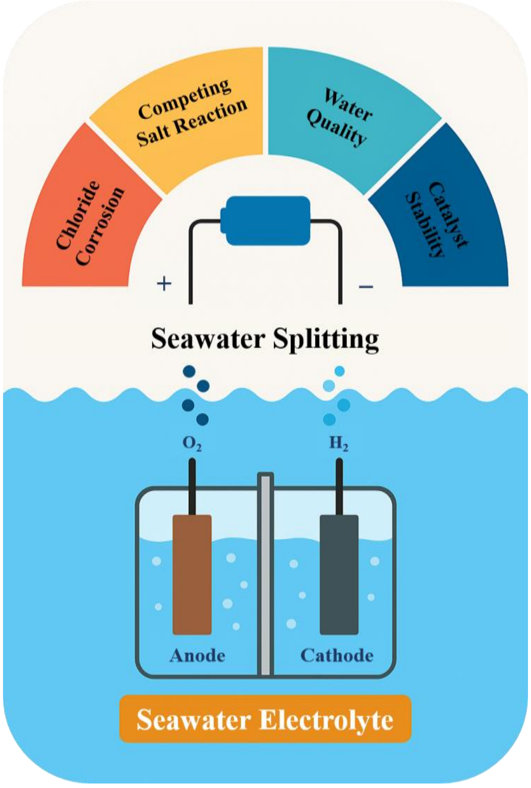

Figure 3. Schematic representation of the seawater electrolysis process and associated challenges.

The lower section illustrates a two-electrode electrolyzer operating in a seawater electrolyte, producing hydrogen (H_2) at the cathode and oxygen (O_2) at the anode. The upper section highlights key obstacles to direct seawater splitting, including chloride corrosion, competing salt reactions, water quality issues, and catalyst stability.

Electrolyzing seawater introduces a host of challenges that are not present in pure water electrolysis. The most critical issues revolve around (1) electrode corrosion and durability, and (2) competing side reactions, both largely stemming from the high chloride content and multicomponent nature of seawater. Additionally, (3) precipitation and fouling at the cathode, and (4) membrane/material stability in the marine environment, are significant concerns. We discuss each of these challenges and their impact on system performance:

Chloride-Induced Corrosion: Chloride is extremely corrosive to most metals when anodically polarized, as it can penetrate passive oxide films and form soluble metal-chloride complexes. In a seawater electrolyzer's anode (which is at high potential), chloride attack can cause rapid dissolution of catalysts and structural materials, including stainless steels and nickel-based alloys commonly used as electrodes. The presence of Cl^- has been shown to drastically shorten electrode lifetimes by pitting corrosion and leaching of active metals [1]. For instance, Ni and Fe oxides (excellent OER catalysts in fresh alkaline water) tend to convert to soluble chlorides or oxychlorides in seawater, losing their active material. Likewise, ion-exchange membranes and cell hardware can degrade due to oxidative chlorine compounds formed in situ. Corrosion not only deactivates the catalyst but also contaminates the product gases (with metal ions or particulates) and poses safety hazards (e.g. structural failure of the electrode). Therefore, enhancing the corrosion resistance of anode catalysts and all exposed materials is paramount. This remains a persistent challenge: even the best-performing direct seawater electrolyzes must ensure that protective measures (material coatings, chemical inhibitors, etc.) keep corrosion rates sufficiently low for long-term operation [16]. As illustrated in Figure 4, in the presence of chloride ions, anodic corrosion and chlorine gas evolution (Cl_2) can co-occur, severely compromising electrode stability and oxygen selectivity.

In addition to inorganic coatings, the use of molecular corrosion inhibitors offers a complementary strategy for mitigating corrosion in chloride-rich environments. For example, optimizing the molecular structure of bio surfactants in acidic chloride media has shown that tuning hydroxyl groups and alkyl chain configurations can promote strong adsorption on steel surfaces and significantly reduce corrosion rates [17]. The development of environmentally benign, green inhibitors tailored for alkaline chloride-containing systems may therefore play an important role in protecting auxiliary components in seawater electrolysis systems in the future. Similarly, the repurposing of expired pharmaceutical compounds such as Remdesivir as corrosion inhibitors for steel in acidic chloride environments has demonstrated that bulky organic molecules with strong surface interaction capabilities can form effective protective layers on metal substrates [18]. Such approaches highlight that the design and upcycling of complex molecular structures can enrich the corrosion mitigation toolbox for seawater-associated electrochemical technologies.

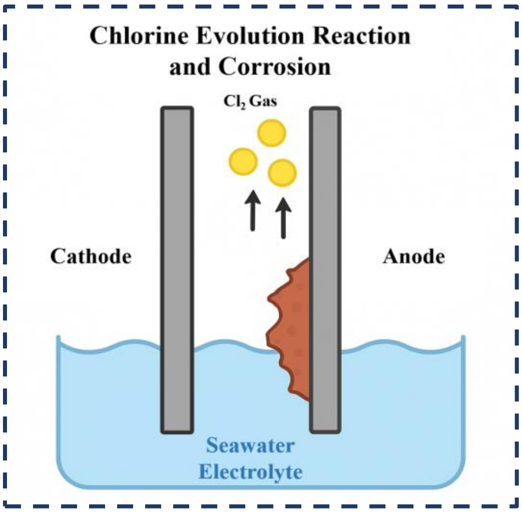

Figure 4. Illustration of the chlorine evolution reaction (CER) and associated anodic corrosion during seawater electrolysis.

Instead of the desired oxygen evolution reaction (OER), chloride ions (Cl^-) in the seawater are oxidized at the anode, generating Cl_2 gas. This parasitic reaction not only reduces the efficiency of hydrogen production but also causes severe corrosion of the anode surface due to the formation of reactive chlorine species.

Competing Side Reactions (Chlorine Evolution): In seawater electrolysis, the desired anodic reaction is oxygen evolution ($4\ OH^- \rightarrow O_2 + 2\ H_2O + 4\ e^-$ in alkaline media). However, chloride can be oxidized via several pathways that compete with or even precede oxygen evolution. One main side reaction is the chlorine evolution reaction (CER): $2\ Cl^- \rightarrow Cl_2 + 2\ e^-$ (in acidic/neutral conditions) or $Cl^- + 2\ OH^- \rightarrow ClO^- + H_2O + 2\ e^-$ (in alkaline, producing hypochlorite) [1]. The standard potential for Cl_2/Cl^- is about 1.36 V vs NHE, which is close to or even lower than OER in many practical conditions, meaning a typical anode will start generating chlorine/hypochlorite as soon as it reaches OER-relevant potentials [1]. Chlorine evolution not only diverts electrons away from OER (reducing efficiency for hydrogen production) but also creates reactive chlorine species that can attack the catalyst and membrane. Chlorine gas is toxic and, if released, poses environmental and safety risks. Moreover, hypochlorite can further react to form chlorate or perchlorate, persistent pollutants that would require careful handling if formed. Therefore, suppressing CER while favoring OER is a central technical hurdle. Ideally, an electro catalyst for the anode should be highly selective for water oxidation even in the presence of high Cl^- concentrations. This selectivity challenge is largely unique to seawater electrolysis and has driven the search for specialized OER catalysts (and operating strategies) that minimize chlorine yields [1].

Cathode Scaling and Precipitation: On the cathode side, the hydrogen evolution reaction ($2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$) generates hydroxide ions that can locally raise pH near the electrode surface. In seawater, the cations such as Mg^{2+} and Ca^{2+} will react with OH^- to form insoluble magnesium hydroxide ($Mg(OH)_2$) and calcium carbonate/hydroxide ($CaCO_3/Ca(OH)_2$) [3]. These precipitates often deposit onto the cathode as a hard scale. $Mg(OH)_2$ in particular forms rapidly when the local pH exceeds ~9.3, which is readily achieved at active cathode sites [3]. The precipitated layer blocks catalytically active surface areas and impedes mass transfer, causing a sharp decline in performance. Once formed, the scale is difficult to remove due to strong adhesion forces (van der Waals and electrostatic) binding it to the electrode [3]. This issue is analogous to limescale buildup in seawater equipment, but accelerated by the high pH micro-environment of the cathode. Without intervention, precipitation can lead to rapid loss of efficiency, requiring higher over potentials to drive the same current and eventually stalling hydrogen production. Thus, maintaining cathode cleanliness is another key challenge. Potential approaches include periodic mechanical or chemical cleaning, or self-cleaning cathode designs (discussed later) that prevent or shed precipitates during operation [3].

Membrane and Component Degradation: In membrane-based electrolyzes (e.g. proton or anion exchange membrane cells), seawater can compromise the membrane and other components. For PEM (acidic) systems, seawater impurities would contaminate catalysts and membranes; hence most seawater research focuses on alkaline systems (AEM or diaphragms). Even so, anion exchange membranes can be attacked by hypochlorite or other oxidants generated from chloride, leading to loss of ion conductivity and mechanical integrity [15]. Plastic or rubber seals and cell frames can also degrade from prolonged exposure to chloride and bromide species. Additionally, multivalent ions like Ca^{2+} and Mg^{2+} can foul membranes by precipitating within their pores or exchanging with functional groups, reducing performance. Ensuring long-term stability of membranes, porous separators, and catalysts in the full chemical milieu of seawater (including trace heavy metals, organics, etc.) is therefore a non-trivial challenge. Testing under real-world conditions over thousands of hours is required to identify failure modes. As noted in a recent review, implementing direct seawater electrolysis remains highly challenging specifically due to “poor catalytic activity and limited lifetime that result from corrosion, chlorine-related side reactions and metal precipitates” [15]. All these factors are interrelated: for example, chlorine generation damages membranes and catalysts; corrosion products can foul membranes; precipitates can create differential concentration cells that enhance corrosion, etc. A successful seawater splitting system must address all of these issues in tandem: corrosion control, side-reaction suppression, precipitation management, and durable construction materials [15].

Recent Advancements in Electro catalysts and System Design

Over the past decade, intensive research efforts have yielded significant advancements in catalyst materials and engineering strategies tailored for seawater electrolysis. Scientists have drawn on innovations in nanomaterials, surface chemistry, and electrochemical engineering to improve both the activity and the robustness of seawater-splitting systems. Here we highlight major developments in electro catalyst design, protective coatings, novel system architectures, and other engineering solutions that address the challenges outlined above. Additionally, recent findings in related energy storage fields highlight the general importance of nanostructured materials and surface modification strategies, demonstrating improved electrochemical performance and enhanced stability across various electrochemical systems [19, 20].

Novel Catalyst Materials for OER and HER in Seawater:

- ✓ **Transition Metal Catalysts with Protective Phases:** One strategy to enhance anode durability is to modify conventional transition metal OER catalysts (Ni, Fe, Co oxides/hydroxides) so they form protective surface layers in situ. Researchers have developed substrate treatments such as suffixation, phosphidation, and salinization of metal electrodes to create a thin layer of metal chalcogenide or phosphide that is more resistant to chloride attack [3]. For example, treating a Ni-based anode to form Ni_3S_2 or Ni_2P on its surface can provide a diffusion barrier against chloride while still allowing water oxidation. These layers can also serve as sacrificial buffers that preferentially react with chloride, preserving the underlying catalyst. Similarly, polyanion coatings (e.g. decorating the catalyst with phosphate or carbonate) have been used to inhibit chloride corrosion [16]. In one approach, a NiFe layered double hydroxide (LDH) catalyst was electrodeposited on a Ni sulfide substrate, forming a hierarchical NiS_x–NiFe LDH structure [3]. During OER, this catalyst in alkaline seawater generated phosphate anions which adsorbed on the surface and helped repel Cl^-, leading to improved stability [3]. These examples illustrate how composite catalysts can combine high OER activity with in-built corrosion mitigation. In parallel, the design of hierarchical super hydrophobic surfaces such as $NiCoTiO_2$ coatings has demonstrated that introducing micro Nano-scale roughness combined with low-surface-energy molecular modification can significantly reduce chloride ion penetration and corrosion rates [23]. Although these results were obtained in non-electrolysis systems, the underlying design principles can be applied to develop durable protective layers for current collectors and auxiliary components in seawater electrolyzes [21].
- ✓ **Layered Double Hydroxides and Anion Intercalation:** LDH materials (e.g. NiFe-LDH, CoFe-LDH) have attracted attention as seawater OER catalysts due to their tunable interlayer chemistry. By intercalating certain anions into the interlayers, the LDH structure can be made more resistant to chloride. A recent study showed that incorporating carbonate (CO_3^{2-}) into CoFe-LDH created strong electrostatic interactions that blocked Cl^- ingress, significantly enhancing the catalyst’s stability in chloride solution [3]. The carbonate-intercalated LDH maintained its structure and activity over extended electrolysis, whereas the carbonate-free form suffered rapid decay. Another innovation is using self-leaching

elements within LDHs: for instance, Al^{3+} was included in a CoFe LDH (forming CoFeAl-LDH). During operation in seawater-like alkaline media, Al^{3+} slowly leached out, leaving behind vacancies that were occupied by hydroxide or carbonate, effectively plugging the sites and creating a self-healing, chloride-resistant matrix [3]. The CoFeAl-LDH anode exhibited excellent stability (voltage decay <0.3% over 500 h) compared to an Al-free LDH which failed rapidly [3]. This "leach-and-protect" mechanism provides a novel route to improve durability: the catalyst sacrifices a benign component (Al) to form protective species in situ. Through such approaches intercalating anions or incorporating labile protective cations LDH-type catalysts have achieved some of the best performances for OER in seawater conditions without noble metals [3].

- ✓ **Nanostructured Transition Metal Catalysts with Carbon Supports:** Recent progress has highlighted the importance of nanostructured electro catalysts in seawater electrolysis, particularly those leveraging transition metals (e.g., Ni, Fe, Co) combined with carbon-based materials. Wang et al. provided an extensive review covering recent advancements in electro catalytic materials specifically tailored for seawater splitting, emphasizing how composite structures, alloying strategies, and surface engineering significantly improve catalyst stability, activity, and resistance to corrosion and fouling in saline conditions [22]. They particularly pointed out that constructing hierarchical nanostructures and employing heterostructures such as metal oxides/hydroxides supported on conductive substrates (carbon nanotubes, graphene, etc.) effectively mitigates chloride-induced corrosion and enhances the electro catalytic selectivity towards water splitting reactions rather than chlorine evolution [22]. For example, hierarchical three-dimensional metal sulfide structures grown on NiCo MXene have been reported as efficient dual-layer electro catalysts, illustrating how 3D architectures can enhance active site exposure, charge transport, and mechanical robustness under harsh electrochemical conditions [23].
- ✓ **Single-Atom and Noble Metal-Doped Catalysts:** While the goal is often to use non-precious catalysts, judicious use of noble metals at atomic scales has shown outsized benefits in seawater splitting. Single-atom catalysts (SACs), where metal atoms like Ir or Ru are isolated on a support, can provide high catalytic activity and unique resistance to poisoning. Intriguingly, recent studies found that certain catalysts can leverage chloride to enhance OER activity rather than be harmed by it [3]. For example, a catalyst consisting of atomically dispersed Ir on a CoFe-LDH support exhibited improved performance in the presence of chloride [3]. The Ir sites formed a mixed hydroxyl–chloride coordination under operation, which actually lowered the OER over potential from 236 mV to 202 mV (at 10 mA cm^{-2}) upon introducing NaCl into the electrolyte [3]. The turnover frequency of O_2 generation increased over sevenfold with an optimal Cl^{-}/ OH^{-} ratio, and the catalyst remained stable for >1000 hours at industrial current densities [3]. This counterintuitive result chloride ions boosting OER was attributed to the formation of an Ir–Cl bond at the active site that modified the electronic structure favorably for oxygen evolution [3]. It demonstrates how engineered active sites can exploit the seawater environment instead of suffering from it. Similarly, noble metal doping can create active centers that are less prone to forming soluble chlorides. Ruthenium or iridium oxides are known for corrosion resistance; when deployed as nanoclusters or single atoms on a corrosion-prone host, they can act as anchors maintaining the activity. The "rare-metal single-atom catalyst" approach holds promise for maximizing performance while minimizing precious metal usage [24].
- ✓ **Cathode Catalysts and Anti-Fouling Designs:** On the hydrogen evolution side, catalysts such as nickel–molybdenum alloys, transition metal phosphides (e.g., Ni_2P, CoP), and transition metal sulfides have been widely investigated as robust HER electro catalysts in alkaline seawater environments [3,11,22]. While HER is generally more facile than OER, a key challenge for seawater-based systems is preventing surface blockage by gas bubbles and inorganic precipitates. Accordingly, recent studies have emphasized cathode architectures that promote efficient bubble release, alleviate concentration gradients, and minimize the adhesion of $Mg(OH)_2$ and Ca-based scales on the active surface [3,22]. Three-dimensional porous electrodes, interconnected channel networks, and wettability-engineered

surfaces have been shown to facilitate rapid detachment and transport of hydrogen bubbles, thereby limiting the residence time of both gas and precipitates at the electrode electrolyte interface [3,22]. Such self-cleaning or anti-fouling designs help maintain accessible active sites, reduce mass-transfer limitations, and sustain low over potentials under prolonged operation.

In parallel, nanostructured and carbon-supported transition metal catalysts further enhance HER performance in seawater-like media. Conductive scaffolds such as carbon nanotubes, graphene, and MXene frameworks improve electron transport and provide mechanically and chemically robust backbones for anchoring active phases. Recent studies on ultra-fast synthesized transition metal MXene nanocomposites for seawater electrolysis have demonstrated low HER over potentials, accelerated charge-transfer kinetics, and excellent durability in saline media, directly confirming the promise of MXene-supported architectures for practical seawater hydrogen production [25]. Recent studies on ultra-fast synthesized transition metal MXene nanocomposites have demonstrated remarkable HER activity and durability in seawater electrolysis, with DFT-supported evidence of enhanced charge-transfer kinetics, suppressed cathodic fouling, and reduced HER over potentials, underscoring their potential for practical seawater hydrogen production [23,25]. Additional mitigation strategies, including optimized flow conditions, periodic current modulation, or polarity reversal, can assist in dislodging adherent deposits, although they must be balanced against energy efficiency considerations. Overall, by rationally coupling catalyst composition with tailored electrode morphology and hydrodynamics, recent work has made substantial progress toward durable, scale-resistant cathodes capable of stable hydrogen generation from seawater [3].

System-Level Engineering Strategies

In parallel with catalyst innovations, system and engineering improvements are crucial to implement seawater splitting at scale:

- ✓ **Membranes and Separators:** Advanced membranes that selectively transport desired ions (H^+, OH^-) while blocking detrimental species (Cl^-, Mg^{2+}) can drastically improve cell life. For example, new AEMs with tuned ion selectivity and chemical resistance to oxidants are being developed specifically for seawater applications. Some designs incorporate a sacrificial antioxidant into the membrane matrix to neutralize chlorine/hypochlorite before it can attack the polymer. Additionally, ceramic or hybrid ion-selective membranes that can tolerate the full salinity of seawater are under exploration. Porous diaphragms (as used in traditional alkaline electrolyzes) are also reconsidered, since they allow some intermixing but are more chemically robust. The choice of membrane ties into whether the system is operated in alkaline mode (AEM or diaphragm) or acidic (PEM which essentially requires pure water, thus less favored for direct seawater). As of now, most direct seawater prototypes are alkaline systems, and progress in anion exchange membrane durability is an active area to ensure long-term operation [15]. In addition, the development of multi-component, water-based intumescent coatings particularly those incorporating fumed silica nanoparticles has suggested that nanostructured additives may contribute to enhanced thermal stability and improved barrier protection [26]. Although such coatings are not designed for electro catalytic functions, the underlying design principles could be relevant to the protection of auxiliary components in seawater electrolysis systems. In this context, these coating strategies might be considered for application to pipelines, storage vessels, current collectors, external frames, and other metallic infrastructure exposed to saline environments, where improved resistance to corrosion and thermal degradation has the potential to support longer service lifetimes.
- ✓ **Multi-Chamber Cell Designs:** As discussed, innovative cell architectures like the three-chamber electrolyzer with dual membranes have shown remarkable effectiveness [3,16]. By physically controlling the environment of each electrode (e.g. keeping anode in a low-chloride environment), these designs eliminate the root cause of many problems. We can expect further refinements, such as asymmetric electrolyzes where the anode and cathode operate at different pH or with different feeds (e.g. anode fed with alkaline water, cathode with seawater). Flow cell designs that continuously flush the electrode surfaces can also help high flow rates on the cathode can sweep away bubbles and precipitates, while flow on the anode can remove any Cl_2 that does form, minimizing its residence time. The trade-off is increased pumping energy, but careful engineering can optimize net efficiency.
- ✓ **Active Control and Sensors:** Smart control systems can enhance seawater

electrolyzer performance. For instance, real-time sensors for detecting chlorine in the anodic compartment could allow dynamic adjustment of voltage or current to avoid reaching the CER onset potential [5]. If chlorine is detected, the system could reduce current or increase the pH (by dosing a base) to suppress it. Similarly, monitoring cell voltage and impedance can give early warning of electrode fouling or membrane degradation, prompting maintenance cycles (e.g. flushing with acid to dissolve precipitates, or injecting inhibitors). The integration of such control strategies will be important in future commercial seawater electrolysis plants to ensure safety (no toxic releases) and reliability.

- ✓ **Integration with Renewable Energy and Marine Infrastructure:** On the macro scale, engineering strategies include where and how seawater electrolyzes are deployed. As mentioned, offshore hydrogen farms coupling wind turbines with seawater electrolysis are being conceived. Demonstrations of floating platforms performing direct seawater electrolysis under ocean conditions (waves, tides) have begun to appear [15]. These require robust system enclosures (to prevent spray and biofouling) and adaptive control to deal with variable power input from renewables. Another concept is to integrate desalination and electrolysis in a hybrid way: for example, using waste heat or by-product oxygen from the electrolyzer to assist a desalination unit, thereby improving overall efficiency of co-located water and hydrogen production. While such integrated designs are complex, they illustrate the creative engineering being applied to make seawater a practical source for hydrogen fuel.

In summary, the landscape of recent advancements is rich: novel electro catalysts are addressing the core chemical issues (corrosion, selectivity, fouling) through material innovations, and system design strategies are providing the engineering solutions (optimized membranes, cell architectures, and operational controls) to implement those advances. The combination of these material and engineering breakthroughs has enabled a direct seawater electrolyzer to operate continuously for over 3200 hours at a current density of 0.25 A cm 2 without failure an achievement that would have seemed improbable a decade ago [16]. In addition to improvements at the catalyst and cell levels, protection of the broader system infrastructure is also essential for long-term deployment. For large seawater-based installations, classical corrosion-mitigation strategies such as cathodic protection can be integrated alongside electrolyzer design. Analytical and numerical studies on mesh-ribbon cathodic protection configurations for above-ground steel structures have shown that optimizing the geometry and arrangement of sacrificial anodes can significantly improve potential distribution and system lifetime [27]. Similar principles can be applied to safeguard storage tanks, pipelines, and metallic support components associated with seawater electrolysis units. Such progress collectively underscores the rapid stride toward practical and durable seawater splitting technology.

Conclusion

Seawater splitting for hydrogen production holds the key to unlocking sustainable, large-scale hydrogen without the burden of freshwater consumption. This review has examined the importance of seawater electrolysis, the challenges that have historically impeded its development, and the recent electro catalytic and engineering advances that are overcoming those barriers. By utilizing seawater (an essentially inexhaustible resource), the hydrogen economy can expand unfettered by water scarcity, ensuring that clean energy goals do not conflict with water security. Environmentally, this means green hydrogen can be produced in coastal and arid regions alike, decarbonizing industries and transport while preserving vital freshwater for other uses [3]. Technologically, the path to efficient seawater electrolysis has demanded innovation on multiple fronts. Researchers have addressed the intertwined problems of corrosion and side reactions by designing catalysts that either resist or even exploit the presence of chloride [3]. Strategies such as protective coatings, anion-intercalated structures, and atomically dispersed catalytic sites have dramatically improved the stability of anode materials in saline media. Likewise, cathode designs that mitigate precipitate buildup have extended operation times by maintaining electrode activity [3]. These advances in materials are matched by clever system designs (from membranes that create selective barriers against impurities to innovative cell layouts that isolate or neutralize problematic species) [3,16]. As a result, the performance gap between seawater and pure-water electrolysis is steadily narrowing.

Despite the progress, challenges remain before seawater splitting is widely commercialized. Long-term durability (beyond thousands of hours) in real seawater conditions, handling of the concentrated brine or by-products, and scaling up production capacity are ongoing considerations. Preventing any environmental harm (such as chlorine leakage or local salinity changes from discharge) will be essential to responsible deployment. However, the trajectory of research is very promising. There is growing optimism that, with continued innovation, direct seawater electrolysis (DSE) can approach the efficiency, safety, and reliability of conventional water electrolysis, particularly in niche coastal and offshore applications [16]. Success in this realm would enable coastal hydrogen plants and offshore energy hubs to flourish, accelerating the transition to a clean energy future.

In conclusion, seawater splitting exemplifies how science and engineering can turn a grand challenge into a transformative opportunity. By harnessing the oceans to produce clean hydrogen fuel, we can address two pressing global issues in tandem (climate change and freshwater scarcity). The advances in electro catalysts and system design highlighted in this review not only solve immediate technical hurdles but also pave the way for sustainable technologies that work in harmony with Earth's natural resources. With continued research and pilot-scale demonstrations, the vision of efficient hydrogen production directly from seawater is on the horizon, promising a new era of green hydrogen that is both environmentally and economically sustainable.

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