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RESEARCH ARTICLE

Recent Advances in Nanostructured Electrocatalysts for Seawater Electrolysis: Towards Sustainable Hydrogen Production

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ABSTRACT - Seawater electrolysis has emerged as a promising and sustainable method for large-scale hydrogen production, utilizing abundant seawater as an alternative to freshwater electrolysis. However, challenges such as catalyst degradation, chloride-induced corrosion, and competition between the oxygen evolution reaction (OER) and chlorine evolution reaction (CER) hinder its widespread adoption. Recent advancements in nanostructured electrocatalysts, including metal-organic frameworks (MOFs), single-atom catalysts (SACs), and transition metal-based alloys, have significantly improved catalytic efficiency, reduced overpotentials, and enhanced stability in harsh marine environments. This review provides a comprehensive analysis of the latest breakthroughs in nanostructured electrocatalysts for seawater electrolysis, with a focus on key material innovations such as nickel-based alloys, molybdenum carbide/phosphide hybrids, and multi-component catalysts optimized for hydrogen evolution reaction (HER) kinetics. Additionally, the role of computational modeling and machine learning in accelerating catalyst design is explored. The economic feasibility and environmental impact of these advanced materials are critically assessed, considering lifecycle analysis, resource sustainability, and industrial scalability. Furthermore, the integration of seawater electrolysis with renewable energy sources, such as offshore wind and solar power, along with hydrogen storage and CO_2 capture strategies, is examined to highlight its potential for a carbon-free energy future. Despite significant progress, challenges remain in enhancing long-term catalyst durability, reducing costs, and achieving large-scale implementation. This review contributes to the ongoing development of sustainable hydrogen production technologies, reinforcing the pivotal role of seawater electrolysis in the global transition toward clean energy.

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1.0 INTRODUCTION

The global energy landscape is shifting towards renewable and sustainable alternatives to mitigate the environmental impact of fossil fuels. Hydrogen has gained significant attention as a clean energy carrier due to its high energy density, zero-emission combustion, and broad applicability in industrial and transportation sectors [1]. Among various hydrogen production methods, water electrolysis powered by renewable energy sources such as solar and wind is considered the most sustainable. However, conventional freshwater electrolysis poses challenges in regions with limited water resources [2].

Seawater electrolysis offers a promising alternative by utilizing the Earth's vast seawater reserves for hydrogen production. Despite its potential, this approach faces key challenges, including catalyst degradation, chloride-induced corrosion, and competition between the OER and CER, which can lead to undesirable chlorine byproducts [2,3]. To address these issues, recent research has focused on nanostructured electrocatalysts that enhance efficiency, selectivity, and stability in seawater electrolysis [4,5].

Nanostructured materials such as MOFs, SACs, and transition metal-based alloys (e.g., NiFe, MoP, and Co-based hybrids) have shown significant improvements in catalytic performance, reducing overpotentials and increasing durability in harsh saline environments [6,7]. Additionally, advancements in electrode morphology and surface engineering have further optimized reaction kinetics and corrosion resistance [8].

This review provides a distinct perspective by not only summarizing recent advancements in nanostructured electrocatalysts for seawater electrolysis but also offering a comparative evaluation of catalyst architectures, surface modifications, and emerging synthesis techniques developed in recent years. Unlike previous reviews, which primarily focus on catalyst performance metrics, this work integrates discussions on recent breakthroughs in nanostructured materials, including metal-organic frameworks (MOFs), single-atom catalysts (SACs), and transition metal-based alloys (e.g., NiFe, MoP, and Co-based hybrids), emphasizing their role in reducing overpotentials and enhancing stability. Additionally, it explores electrode morphology and interface engineering, highlighting how surface modifications and novel structural designs contribute to improved reaction kinetics and corrosion resistance [9-11].

Beyond material advancements, this review examines the techno-economic feasibility and scalability of seawater electrolysis by discussing its integration with renewable energy technologies, economic considerations, and pathways toward commercialization—an area often overlooked in prior reviews. Furthermore, it identifies gaps in the current understanding of electrocatalyst degradation mechanisms and proposes strategies for next-generation catalyst development. By addressing both the fundamental challenges and the broader system-level integration of seawater electrolysis, this review offers a more holistic and forward-looking analysis compared to existing literature. The insights presented here contribute to advancing the development of next-generation electrocatalysts for large-scale, cost-effective, and environmentally sustainable hydrogen production from seawater.

1.1 IMPORTANCE OF SEAWATER ELECTROLYSIS IN SUSTAINABLE HYDROGEN PRODUCTION

Hydrogen is increasingly recognized as a crucial enabler of the global transition to clean energy, providing a sustainable alternative to fossil fuels for industrial processes, power generation, and transportation. Conventional hydrogen production methods, such as steam methane reforming (SMR), are highly carbon-intensive, whereas water electrolysis offers a pathway to "green hydrogen" when powered by renewable energy sources [1]. However, freshwater electrolysis requires large amounts of purified water, which is scarce in many regions. Seawater electrolysis presents a viable alternative, utilizing the Earth's vast seawater reserves for hydrogen production in an environmentally sustainable manner [3].

Freshwater scarcity is a growing global concern, particularly in arid and semi-arid regions where access to clean water is limited. Traditional electrolysis competes with drinking water and agricultural demands, whereas seawater electrolysis eliminates the need for freshwater, enabling large-scale hydrogen production without straining essential water resources [1,3]. This approach is particularly advantageous for coastal regions and island nations, where seawater is abundant, and desalination is both energy-intensive and costly.

When powered by renewable energy, seawater electrolysis significantly reduces carbon emissions compared to fossil fuel-based hydrogen production methods [5]. Unlike SMR, which releases substantial CO_2, seawater electrolysis produces hydrogen without greenhouse gas emissions. Moreover, integrating seawater electrolysis with offshore wind farms and floating solar farms enables decentralized, scalable hydrogen production, enhancing energy security and reducing reliance on fossil fuels [1,7].

Despite its potential, seawater electrolysis faces technical challenges, primarily due to the corrosive nature of seawater and competition between the oxygen evolution reaction (OER) and chlorine evolution reaction (CER) [2,3]. Chloride ions accelerate electrode degradation and lead to the formation of toxic chlorine byproducts. To address these issues, researchers are developing nanostructured electrocatalysts, such as nickel-based alloys, molybdenum carbide/phosphide hybrids, and metal-organic frameworks (MOFs), which enhance catalytic efficiency, improve corrosion resistance, and increase OER selectivity over CER [5-7].

From an economic standpoint, seawater electrolysis has the potential to lower hydrogen production costs by leveraging freely available seawater resources. Advances in electrocatalyst design and scalable electrolyzer technologies are making seawater electrolysis increasingly competitive with conventional hydrogen production methods [9]. Industrial sectors such as ammonia synthesis, steel manufacturing, and fuel cell technologies could benefit from on-site green hydrogen production via seawater electrolysis, reducing dependence on imported fossil fuels [10].

1.2 COMPARISON OF SEAWATER ELECTROLYSIS WITH FRESHWATER ELECTROLYSIS

Hydrogen production via water electrolysis is a well-established method that, when powered by renewable energy, enables the generation of green hydrogen. However, conventional freshwater electrolysis requires highly purified water, limiting its feasibility in water-scarce regions. Seawater electrolysis presents an attractive alternative due to the vast availability of seawater. Despite its advantages, it introduces technical challenges, particularly regarding electrode stability and byproduct formation [1,2]. This section compares freshwater and seawater electrolysis based on key parameters, including resource availability, energy efficiency, technical challenges, and economic considerations.

Parameter	**Freshwater Electrolysis**	**Seawater Electrolysis**
Water Source	Requires purified freshwater, often obtained through energy-intensive processes such as desalination [1].	Utilizes abundant seawater, eliminating competition with drinking water and agriculture [2].
Electrolyte Composition	Typically, alkaline (KOH) or acidic (H_2SO_4) electrolytes to enhance conductivity and efficiency [6].	Contains high concentrations of chloride ions (Cl^-) and other impurities, leading to electrode corrosion and side reactions [2,5].
Competing Reactions	Predominantly oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) with high selectivity [3].	Chlorine evolution reaction (CER) competes with OER, producing harmful chlorine byproducts [2,7].
Electrode Stability	Less corrosive environment, leading to longer electrode lifespan [6].	Requires highly corrosion-resistant electrodes due to chloride-induced degradation [5].
Catalyst Requirements	Precious metals (Pt, Ru, Ir) or non-precious metal oxides (NiFe, Co-based) with optimized activity and stability [9].	Advanced nanostructured electrocatalysts such as MOFs, single-atom catalysts, and metal alloys to enhance stability in seawater [4-7].
Energy Efficiency	Lower overpotential, leading to higher efficiency [6].	Higher overpotential required due to side reactions and corrosion effects, reducing efficiency [1,8].
Environmental Impact	Requires freshwater resources, which can be scarce and may lead to ecosystem disruption if over-extracted [2].	Reduces dependence on freshwater, but care must be taken to prevent chlorine pollution and electrode degradation waste [1,8].
Economic Viability	Established industrial technology, widely used with commercialized electrolysers [9].	Requires further research and technological advancements to improve durability and efficiency before large-scale deployment [2,10].

Seawater electrolysis holds great potential for large-scale hydrogen production, but challenges such as electrode stability, selectivity against chlorine evolution, and overall energy efficiency must be addressed. Advancements in nanostructured electrocatalysts and system integration with renewable energy sources are crucial to making seawater electrolysis a commercially viable solution for sustainable hydrogen production [2,5].

2.0 OVERVIEW OF SEAWATER ELECTROLYSIS

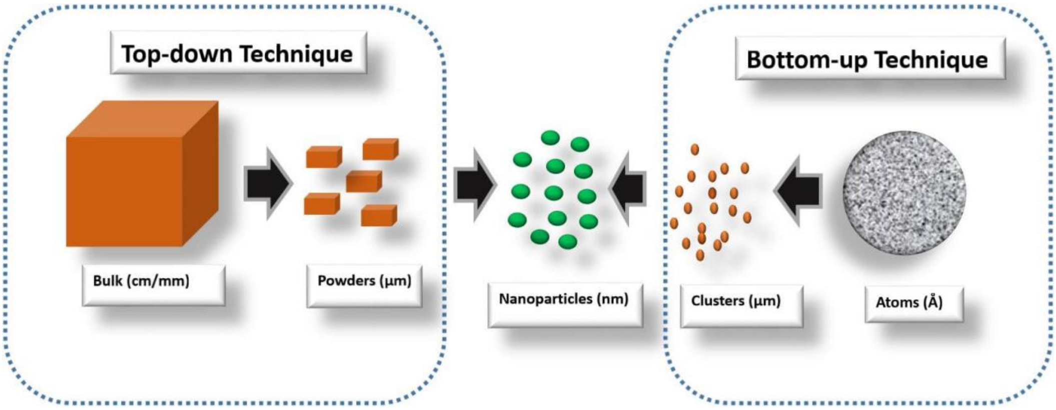

Figure 1. Seawater Electrolysis

2.1 IMPORTANCE OF SEAWATER ELECTROLYSIS IN SUSTAINABLE HYDROGEN PRODUCTION

Seawater electrolysis has emerged as a key technology for sustainable hydrogen production, offering a renewable, cost-effective, and environmentally friendly alternative to conventional hydrogen production methods. Unlike traditional water electrolysis, which relies on high-purity freshwater, seawater electrolysis utilizes Earth's vast and abundant oceanic resources, which constitute approximately 97% of the planet’s water supply, to generate green hydrogen without exacerbating freshwater scarcity [11]. This approach addresses critical global challenges by alleviating freshwater stress, particularly in arid regions, where water availability is a growing concern due to climate change and rising demand. Additionally, seawater electrolysis can be integrated with renewable energy sources such as solar, wind, and tidal energy, further enhancing its sustainability as a hydrogen production pathway. Some advanced systems even offer dual functionality, simultaneously generating hydrogen and desalinating seawater, providing a synergistic solution for clean energy and freshwater production [11]. Moreover, by shifting hydrogen production away from fossil fuel-based methods, seawater electrolysis plays a crucial role in reducing CO_2 emissions and supporting global decarbonization efforts. However, despite its potential, seawater electrolysis faces significant challenges, including chloride-induced corrosion, competing side reactions such as the chlorine evolution reaction (CER), and electrode stability issues. Addressing these challenges requires the development of advanced nanostructured electrocatalysts to enhance efficiency, selectivity, and durability, ensuring the feasibility of seawater electrolysis for large-scale hydrogen production [11].

2.2 COMPARISON OF SEAWATER ELECTROLYSIS WITH FRESHWATER ELECTROLYSIS

Seawater electrolysis presents a promising alternative to freshwater electrolysis for large-scale, sustainable hydrogen production. While it eliminates freshwater dependency, it introduces challenges such as chloride-induced corrosion and competing side reactions. The following comparison highlights key differences between the two methods across critical parameters:

1. Feedstock Availability & Sustainability

   Freshwater electrolysis requires purified water, which can be limited in arid regions and often competes with drinking water and agriculture. In contrast, seawater electrolysis utilizes the Earth's abundant seawater reserves, covering approximately 97% of the planet’s water supply. This makes seawater electrolysis a more sustainable option, as it does not deplete freshwater resources. Additionally, freshwater electrolysis often necessitates energy-intensive purification processes, whereas seawater electrolysis can operate directly with seawater, reducing the need for desalination.

2. Electrolyte Composition & Side Reactions

   Freshwater electrolysis primarily uses high-purity water with minimal impurities, allowing for efficient hydrogen evolution. Seawater, however, contains a complex mixture of salts and minerals, including NaCl, Mg^{2+}, Ca^{2+}, and SO_4^{2-}, which introduce challenges such as unwanted side reactions. A major issue in seawater electrolysis is the competing chlorine evolution reaction (CER), which produces Cl_2 gas. This reaction not only reduces efficiency but also leads to corrosion and environmental safety concerns [2].

3. Electrode Stability & Corrosion Resistance

   Electrode stability is a significant challenge in seawater electrolysis due to the highly corrosive environment created by chloride ions. Freshwater electrolysis operates in less aggressive conditions, leading to longer electrode lifespans. In contrast, seawater electrolysis requires corrosion-resistant electrodes, often developed using advanced nanostructured materials such as CoPx@FeOOH and NiFe-MOFs, which enhance stability and prevent electrode degradation [1,2].

4. Energy Efficiency & Overpotential Requirements

The standard water-splitting potential for electrolysis is 1.23V for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Freshwater electrolysis typically operates near this potential, with minor additional overpotential required for efficiency optimization. Seawater electrolysis, however, requires an additional overpotential of approximately 0.2-0.4V due to the presence of competing ClER and ionic impurities [2,11]. To enhance efficiency, seawater electrolysis demands highly selective electrocatalysts that suppress ClER while promoting OER, ensuring efficient hydrogen production.

5. Practical Applications & Cost Considerations

Freshwater electrolysis is widely used in commercial alkaline and PEM electrolyzers for green hydrogen production, but its dependence on high-purity water increases operational costs. Seawater electrolysis, on the other hand, is an emerging technology with significant potential for coastal, offshore, and island-based hydrogen production [1]. By eliminating the need for destruction, seawater electrolysis reduces water purification costs. However, it requires advanced electrocatalysts to improve durability and efficiency, adding to the overall development costs [11].

Despite these challenges, recent advancements in nanostructured electrocatalysts—including graphene-based catalysts, MOF-derived materials, and single-atom catalysts—are significantly improving the efficiency, selectivity, and durability of seawater electrolysis [4,5,12]. These innovations are paving the way for the large-scale implementation of seawater electrolysis, making it a viable solution for sustainable hydrogen production in the future.

3.0 TYPES OF NANOSTRUCTURED ELECTROCATALYSTS

Nanostructured electrocatalysts play a crucial role in seawater electrolysis by enhancing catalytic efficiency, stability, and selectivity while mitigating challenges such as chloride corrosion and competing side reactions [2]. These materials can be broadly classified into several categories, including carbon-based materials (e.g., graphene), MOFs, single-atom catalysts, and transition metal compounds such as phosphides, oxides, and carbides [3]. Their synthesis methods vary, with hydrothermal synthesis, electrodeposition, chemical vapor deposition (CVD), solvothermal techniques, and templated synthesis being the most common approaches [13]. Among these, graphene-based electrocatalysts have gained significant attention due to their excellent conductivity, large surface area, tunable electronic properties, and exceptional corrosion resistance, making them highly effective for the HER and OER in seawater electrolysis [14].

3.1 GRAPHENE-BASED ELECTROCATALYSTS

Graphene-based electrocatalysts have emerged as a promising class of materials for seawater electrolysis due to their ability to enhance electron transport, increase active surface sites, and improve catalytic efficiency [12]. The sp^2 hybridized carbon lattice of graphene provides high mechanical stability, making it an excellent support material for transition metals, heteroatoms, and single-atom catalysts [15]. Some key advantages of graphene-based electrocatalysts include their high surface area, which allows for better dispersion of active sites and improved catalytic efficiency; superior electrical conductivity that enhances electron transfer kinetics, reducing energy losses during electrolysis; excellent corrosion resistance that ensures stability in harsh seawater conditions by mitigating chloride-induced degradation; and tunable properties that enable functionalization with heteroatoms (e.g., nitrogen, phosphorus, sulfur) or metal doping to enhance HER and OER performance [13-15].

Several synthesis approaches are used to develop graphene-based electrocatalysts. Chemical vapor deposition (CVD) is widely employed to produce high-purity graphene films with controllable thickness and defect levels, while hydrothermal and solvothermal synthesis methods are commonly used to integrate graphene with metal nanoparticles or introduce heteroatom doping. Electrochemical exfoliation generates defect-rich graphene with enhanced catalytic activity, and thermal reduction of graphene oxide (GO) is another effective approach for improving conductivity by removing oxygen functional groups. Additionally, self-assembly and template-assisted growth techniques enable the formation of hierarchical structures with optimized porosity and charge transfer pathways [12].

Recent studies have demonstrated the potential of graphene-supported transition metal catalysts, such as NiFe layered double hydroxides (LDHs), Co-based phosphides, and Mo-based carbides, in improving the efficiency of seawater electrolysis. Single-atom catalysts anchored on graphene frameworks have also exhibited remarkable catalytic activity by maximizing atomic utilization while maintaining long-term stability. For example, graphene-supported NiFe LDH catalysts have been reported to exhibit an OER overpotential of just 287 mV at 1000 mA cm^{-2}, making them highly efficient anode materials for direct seawater electrolysis [2]. Similarly, CoPx@FeOOH core-shell structures on graphene supports have demonstrated high HER activity while effectively suppressing chloride corrosion [16].

3.2 METAL-ORGANIC FRAMEWORKS (MOFS) AS ELECTROCATALYSTS

Metal-organic frameworks (MOFs) have also emerged as a promising class of nanostructured electrocatalysts for seawater electrolysis due to their high porosity, tunable structure, and exceptional catalytic properties. Their unique framework, consisting of metal nodes coordinated with organic linkers, provides an ultrahigh surface area, abundant active sites, and excellent ion transport channels, making them ideal for HER and OER in seawater splitting. The key advantages of MOF-based electrocatalysts include their high surface area and porosity, which enhance mass transport of reactants and intermediates, thereby improving overall reaction kinetics; structural tunability, which allows fine-tuning of catalytic activity and selectivity by modifying metal centers and organic linkers; abundant active sites, particularly metal clusters (e.g., Co, Ni, Fe) and nitrogen-rich linkers, which enhance HER and OER performance; and the ability of MOFs to serve as self-sacrificial templates, enabling their transformation into metal oxides, carbides, phosphides, or single-atom catalysts, further improving their stability and activity in seawater electrolysis [4].

Despite these advantages, pristine MOFs often suffer from low electrical conductivity and limited stability under harsh electrochemical conditions. To address these limitations, researchers have developed MOF composites and derivatives with significantly enhanced catalytic performance. Various synthesis strategies have been explored for MOF-based electrocatalysts. Hydrothermal and solvothermal synthesis methods involve reacting metal salts with organic linkers under controlled temperature and pressure conditions to form highly crystalline structures with tunable pore sizes. Direct pyrolysis of MOFs can convert them into metal/nitrogen-doped carbon catalysts (M-N-C), metal oxides, or phosphides, thereby enhancing conductivity and stability. In situ growth on conductive supports, such as carbon paper, graphene, or nickel foam, improves charge transfer and mechanical stability, while metal doping and hybridization strategies incorporating additional metal atoms (e.g., Ni, Fe, Mo) enhance bifunctional electrocatalytic activity for both HER and OER. For example, NiFe-MOFs have demonstrated exceptional OER efficiency in alkaline seawater conditions.

Recent studies have highlighted the effectiveness of MOF-derived catalysts in addressing key challenges of seawater electrolysis, including chloride corrosion resistance, high current density operation, and long-term stability. MOF-derived cobalt phosphide (CoP) catalysts have exhibited high intrinsic activity and durability in alkaline seawater due to their strong Co-P bonding, which enhances HER kinetics. Additionally, NiFe-MOFs have been reported to exhibit an OER overpotential as low as 296 mV at 1000 mA cm^{-2}, making them highly efficient anode materials for direct seawater splitting. Furthermore, single-atom catalysts (SACs) derived from MOFs, such as Fe-SACs and Co-SACs anchored on nitrogen-doped graphene, have demonstrated exceptional stability and activity, achieving high turnover frequencies (TOF) and long-term durability in real seawater conditions. These advancements underscore the potential of MOF-based electrocatalysts in revolutionizing seawater electrolysis for sustainable hydrogen production [4].

4.0 PERFORMANCE METRICS

4.1 ANALYSIS OF KEY PERFORMANCE METRICS FOR ELECTROCATALYSTS, INCLUDING ACTIVITY, STABILITY, AND SELECTIVITY

The efficiency of an electrocatalyst in promoting the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) is determined by its ability to minimize the energy required for these processes. A highly active catalyst is characterized by a low overpotential, which allows the reactions to occur with minimal energy loss. For instance, NiFe-layered double hydroxide (NiFe-LDH) catalysts exhibit an overpotential of approximately 280 mV at a current density of 10 mA cm^{-2} for OER, making them particularly effective for seawater oxidation [11]. Similarly, MoS_2 modified with dual metal atoms enhances HER kinetics and reduces overpotential by improving electronic conductivity [14]. The Tafel slope is commonly used to assess activity; lower Tafel slopes indicate more efficient charge transfer and faster reaction rates, both of which are crucial for optimizing water-splitting efficiency [1].

Stability is critical for ensuring long-term electrocatalytic performance, especially in corrosive seawater environments where exposure to chloride ions (Cl^-) and fluctuating pH levels can cause catalyst degradation. Chronoamperometry and chronopotentiometry are frequently used to evaluate the durability of electrocatalysts over extended periods of operation [9]. For example, molybdenum carbide/phosphide hybrid nanoparticles embedded in P, N co-doped carbon nanofibers have shown exceptional stability for over 100 hours during seawater electrolysis, thanks to their strong corrosion resistance [6]. Likewise, alloyed nickel-based electrodes have demonstrated prolonged durability by minimizing surface oxidation and maintaining catalytic performance over extended use [7]. To enhance catalyst longevity, protective coatings, nanostructuring, and doping strategies have been employed in real-world applications [1].

Selectivity ensures that the catalyst predominantly facilitates HER and OER while minimizing side reactions, particularly the chlorine evolution reaction (ClER) in seawater electrolysis. High selectivity reduces energy losses and improves hydrogen purity. Strategies such as surface modifications, heteroatom doping, and core-shell catalyst designs have been employed to enhance selectivity [2,11]. For example, core-shell CoPx@FeOOH catalysts demonstrate improved OER selectivity by shifting reaction pathways away from ClER, making them highly effective for seawater splitting [16]. Additionally, small-molecule oxidation-assisted seawater electrolysis has been proposed as a strategy to suppress ClER and thereby improve overall system efficiency and selectivity [16]. Techniques like faradaic efficiency measurements, in-situ spectroscopic analysis, and gas chromatography are essential for evaluating selectivity, as they allow for the quantification of reaction products and confirmation of suppressed side reactions [13].

4.2 EVALUATING ELECTROCATALYST PERFORMANCE IN REAL SEAWATER CONDITIONS

Evaluating electrocatalyst performance under real seawater conditions requires a comprehensive approach that considers stability, corrosion resistance, selectivity, and efficiency. Unlike laboratory-prepared electrolytes, natural seawater contains high concentrations of chloride ions (Cl^-), fluctuating pH levels, organic impurities, and dissolved oxygen, all of which can contribute to severe electrode degradation and unwanted side reactions, such as ClER [10]. To accurately assess catalytic performance, faradaic efficiency, gas purity analysis, and stability testing are essential. Faradaic efficiency measures the proportion of total charge used in the desired HER/OER reactions compared to side reactions. Studies have shown that core-shell structured catalysts like CoPx@FeOOH exhibit high faradaic efficiency by selectively suppressing ClER while promoting OER in seawater electrolysis [9, 13]. Furthermore, gas chromatography and online mass spectrometry are frequently employed to analyze the purity of evolved hydrogen and oxygen, ensuring minimal chlorine contamination [14].

Stability and durability assessments are critical for ensuring the long-term operation of electrocatalysts in real seawater. Techniques such as chronoamperometry, chronopotentiometry, and electrochemical impedance spectroscopy (EIS) are used to monitor catalyst degradation, surface restructuring, and changes in resistance over time [15]. For instance, alloyed nickel-based electrodes have demonstrated remarkable stability by maintaining consistent current densities and minimal overpotential shifts after over 100 hours of continuous operation in real seawater [7]. Advanced in-situ characterization techniques, such as X-ray absorption spectroscopy (XAS), Raman spectroscopy, and scanning electrochemical microscopy (SECM), provide real-time insights into catalyst behavior under actual seawater conditions [5]. Moreover, computational simulations and machine learning models are increasingly utilized to predict degradation mechanisms and optimize catalyst composition before experimental validation [9]. These combined evaluation strategies are crucial for identifying and developing robust, corrosion-resistant electrocatalysts that can sustain high-efficiency seawater electrolysis for long-term hydrogen production.

5.0 MECHANISMS OF CATALYSIS

Seawater electrolysis is a promising yet challenging approach for hydrogen production, primarily due to the presence of chloride ions (Cl^-), which can trigger the unwanted chlorine evolution reaction (CER) alongside the desired oxygen evolution reaction (OER). The implementation of nanostructured electrocatalysts significantly improves reaction kinetics and enhances overall system durability by optimizing catalytic efficiency and selectivity. Nanostructured electrocatalysts improve seawater electrolysis performance by reducing overpotential, increasing active sites, enhancing stability, and improving selectivity. Advanced nanomaterials lower the required voltage for hydrogen evolution reaction (HER) and OER, thus enhancing energy efficiency [9]. High surface-area nanostructures expose more catalytic sites, which increases the reaction rates [12]. Corrosion-resistant nanomaterials prevent chloride-induced degradation, ensuring long-term catalytic performance [8], while selective catalysts suppress CER while promoting OER, enabling high-purity hydrogen production [14]. Recent studies highlight that transition metal-based nanostructures such as Ni-Fe layered double hydroxides (LDHs), graphene-supported catalysts, and metal-organic frameworks (MOFs) effectively lower energy barriers while preventing chloride degradation [12]. Moreover, core-shell nanostructures and single-atom catalysts demonstrate improved OER selectivity due to optimized charge transfer properties [10].

5.1 ROLE OF SURFACE AREA, POROSITY, AND ELECTRONIC PROPERTIES IN ENHANCING CATALYTIC ACTIVITY

1. Surface Area and Active Site Exposure

The electrochemical active surface area (ECSA) plays a critical role in electrocatalytic efficiency, as a higher ECSA increases the number of active sites available for reaction intermediates. This effect is particularly evident in graphene-based catalysts, which exhibit high electron mobility and tunable surface properties that enhance HER activity [12]. Additionally, core-shell nanostructures expose multiple reactive planes, further increasing catalytic activity [8]. Experimental studies indicate that catalysts with high ECSA (>200 m^2/g) demonstrate improved HER kinetics, leading to lower overpotentials and higher current densities [10].

2. Porosity and Mass Transport Efficiency

Porous nanostructures significantly improve mass transport properties by allowing better diffusion of electrolyte species and reducing ion transport resistance. Hierarchical porosity in MOF-derived catalysts enhances reactant diffusion and prevents gas bubble accumulation, which can hinder electrocatalytic efficiency [16]. For instance, MOF-derived Ni-Fe catalysts with a porosity >0.5 cm^3/g exhibit a current density exceeding 100 mA/cm^2 at 1.6 V vs. RHE [12]. Nanoporous metal-oxide catalysts demonstrate superior OER performance, particularly at high current densities, due to their ability to facilitate rapid electrolyte penetration [8].

3. Electronic Properties and Charge Transfer Efficiency

The electronic conductivity of an electrocatalyst significantly influences charge transport and overall reaction rates. High-conductivity materials such as doped graphene and transition metal phosphides facilitate faster electron transfer, thereby reducing charge accumulation and improving HER efficiency [10]. Studies show that graphene-supported catalysts exhibit a conductivity exceeding 100 S/cm, which enhances their electrocatalytic response under alkaline and saline conditions [12].

4. Optimizing Catalytic Morphology

The morphology and crystalline structure of an electrocatalyst can significantly influence its performance. Optimizing facet exposure and defect engineering improves catalytic efficiency by altering reaction pathways and increasing active site availability [8]. Tuning facet exposure, such as adjusting the {111} vs. {100} planes, modifies adsorption energies and enhances catalytic selectivity [12]. Recent reports indicate that single-atom catalysts with precisely controlled coordination environments achieve overpotentials as low as 180 mV for OER, significantly outperforming conventional transition metal catalysts [5].

Table 1: Summary of Key Electrocatalysts for Seawater Electrolysis

Electrocatalyst	**Advantages**	**Limitations**	**References**
Ni-Fe LDHs	High OER activity, enhanced charge transfer	Limited long-term stability in saline environments	[12, 14]
Graphene-supported catalysts	High surface area, excellent electron conductivity	Complex synthesis, potential agglomeration	[8, 12]
Metal-organic frameworks (MOFs)	Tunable porosity, enhanced mass transport	Structural instability under prolonged operation	[10, 16]
Ni-Co phosphides	High HER activity, good electrochemical stability	Prone to surface oxidation in chloride environments	[10]
Single-atom catalysts (SACs)	Optimized charge transfer, superior catalytic efficiency	High cost, challenging synthesis and scale-up	[5, 17]
Core-shell nanostructures	Improved selectivity, corrosion resistance	Complexity in fabrication, potential structural degradation	[10]

6.0 STABILITY AND DURABILITY

6.1 CHALLENGES RELATED TO THE STABILITY AND DURABILITY OF NANOSTRUCTURED ELECTROCATALYSTS IN SEAWATER ENVIRONMENTS

Nanostructured electrocatalysts employed in seawater electrolysis face significant stability challenges due to the corrosive marine environment, which is characterized by high salinity, chloride ion attack, and electrochemical degradation [5]. The presence of aggressive chloride ions (Cl^-) accelerates the structural deterioration of electrocatalysts, leading to catalyst deactivation and decreased operational efficiency over time [2]. One primary issue that negatively affects catalyst durability is metal leaching, especially in transition metal-based catalysts such as Ni, Fe, and Co. These metals tend to dissolve during prolonged electrolysis, thus reducing their catalytic effectiveness [8]. Another challenge is nanoparticle aggregation, as smaller catalytic particles tend to cluster and form larger agglomerates. This aggregation reduces the active surface area, diminishing the overall efficiency of the catalyst [5]. Additionally, single-atom catalysts (SACs), despite their high intrinsic catalytic activity, are prone to migration and clustering, resulting in a rapid loss of active sites [5]. The dissolution of metal nanoparticles into the electrolyte further exacerbates performance decay, ultimately limiting the long-term applicability of these materials in seawater electrolysis [2]. Electrocatalyst degradation is often caused by electrode passivation, wherein insoluble metal oxides and hydroxides form a protective but non-conductive layer. This layer increases overpotential and reduces efficiency [1]. Furthermore, hydroxyl and hypochlorite radicals, which are byproducts of seawater electrolysis, contribute to the structural degradation of catalytic materials, accelerating their breakdown. Metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), often used for spatially confining metal atoms, also face degradation in alkaline seawater environments, leading to hydrolysis and framework collapse. This further limits the catalyst's longevity [4].

The continuous exposure of electrocatalysts to seawater conditions results in severe electrochemical and chemical degradation, which impacts both oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) efficiency [10]. Studies on Ni-Fe-based catalysts indicate that surface oxidation in chloride-rich environments leads to phase transitions that negatively affect the conductivity and reactivity of the catalysts [2]. Prolonged operation at high current densities leads to the formation of metal hydroxides that block active sites and reduce mass transport, ultimately lowering efficiency [8]. This issue is particularly prominent in high-performance HER catalysts, such as MoS_2 and Ni-Mo alloys, which suffer from surface restructuring and a decline in catalytic activity under the harsh conditions of alkaline seawater [11].

6.2 STRATEGIES TO ENHANCE THE LIFETIME OF ELECTROCATALYSTS

To address the stability issues and extend the lifetime of nanostructured electrocatalysts in seawater electrolysis, various engineering strategies have been developed. These strategies include surface modifications, core-shell architectures, and tuning of electronic structures to improve catalytic durability and resistance to corrosion [9].

1. Core-Shell Structures for Corrosion Resistance

   One of the most effective strategies for enhancing stability involves the design of core-shell nanostructures, where a chemically stable shell, such as TiO_2, MoS_2, or carbon-based layers, protects the active core from chloride attack and dissolution [8]. These core-shell catalysts not only improve the stability of the electrocatalysts but also maintain high catalytic performance by preventing direct contact between the reactive core and corrosive seawater components [2].

2. Alloying and Doping Strategies for Enhanced Stability

   Alloying transition metals, such as Ni-Co and Ni-Mo, has been shown to significantly improve the long-term electrochemical stability of catalysts. These alloys exhibit enhanced resistance to chloride-induced corrosion compared to monometallic catalysts [11]. Additionally, heteroatom doping, especially N, P, and S doping in carbon-based materials, has been found to further enhance the electronic structure of electrocatalysts, thereby improving their catalytic durability and corrosion resistance [5]. Defect engineering also plays a crucial role by introducing stable active sites through controlled vacancy concentrations in metal oxides, which helps prevent catalyst degradation and ensures long-term operational efficiency [2].

3. Carbon-Based Supports and Protective Coatings

   The use of graphene-based conductive supports has been widely adopted to prevent nanoparticle aggregation and metal leaching. Graphene provides structural stability while enhancing charge transfer efficiency, which improves the overall stability of the electrocatalyst [13]. Recent advancements in covalent organic frameworks (COFs) have demonstrated their effectiveness in anchoring single-atom catalysts (SACs), thereby preventing their mobility and enhancing long-term durability [4]. Furthermore, hydrophobic surface treatments have been employed to reduce excessive water adsorption, thereby minimizing electrode delamination and surface degradation [1].

4. Machine Learning and Computational Approaches for Catalyst Optimization

Machine learning and density functional theory (DFT) simulations are increasingly being utilized to predict degradation pathways and optimize catalyst compositions before large-scale experimental validation [9]. These computational methods allow for the rapid screening of high-performance, corrosion-resistant materials, thus accelerating the development of next-generation durable electrocatalysts [11]. The combination of protective coatings, alloy engineering, carbon-based supports, and computational modeling is essential to ensuring the long-term stability of nanostructured electrocatalysts in seawater electrolysis. These strategies mitigate catalyst degradation, prolong operational lifetimes, and enable the scalability of seawater electrolysis for industrial-scale green hydrogen production [5].

7.0 ENVIRONMENTAL AND ECONOMIC CONSIDERATIONS

7.1 ENVIRONMENTAL IMPACT OF USING NANOSTRUCTURED MATERIALS AND LIFECYCLE ANALYSIS

The use of nanostructured electrocatalysts in seawater electrolysis offers both environmental benefits and challenges. On one hand, these advanced materials significantly enhance the efficiency of hydrogen production by reducing energy losses and improving the kinetics of both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [10]. A notable environmental advantage is their ability to operate in seawater, eliminating the need for freshwater resources and thus reducing the pressure on already limited freshwater supplies [2]. This makes seawater electrolysis an attractive and sustainable alternative to freshwater-based systems.

However, there are several environmental concerns related to the lifecycle of these nanostructured materials. The synthesis of metal-based nanomaterials, such as nickel-based alloys and molybdenum carbide/phosphide hybrids, often involves energy-intensive processes and the use of hazardous chemicals, which could lead to environmental pollution if not properly managed [6,7]. In addition, the long-term stability of these catalysts in real-world seawater conditions remains a significant challenge. The degradation and leaching of metal ions, such as Ni, Co, and Mo, into marine ecosystems could result in toxicity and bioaccumulation, posing potential risks to marine life [5]. To address these issues, ongoing research is focused on developing recyclable and eco-friendly electrocatalysts, such as single-atom catalysts (SACs) and metal-organic frameworks (MOFs), which are expected to mitigate these environmental concerns [4,5].

Lifecycle analysis (LCA) studies have indicated that nanostructured electrocatalysts generally have a lower operational energy footprint compared to conventional platinum-based systems, offering a more sustainable solution for large-scale hydrogen production. However, their production-phase environmental impact remains a challenge due to the need for high-purity raw materials and the complexity of fabrication techniques [9]. Sustainable synthesis methods, including green chemistry approaches and waste recycling, are being explored to minimize these environmental impacts and promote the overall sustainability of seawater electrolysis technologies [8].

7.2 ECONOMIC VIABILITY AND SCALABILITY OF NANOSTRUCTURED ELECTROCATALYSTS

The economic feasibility of large-scale hydrogen production via seawater electrolysis heavily depends on the cost-effectiveness and durability of the electrocatalysts used. Traditionally, platinum-group metals (PGMs) have been the most efficient catalysts for HER and OER. However, the high cost and scarcity of these metals hinder their widespread adoption for large-scale hydrogen production [7]. In contrast, nanostructured alternatives, such as NiFe-layered double hydroxides, Mo-based hybrids, and alloyed nickel-based electrodes, offer a more cost-effective solution while maintaining high catalytic performance, thus presenting an attractive option for large-scale applications [5-7].

Scalability remains a significant challenge, particularly in ensuring the stability and corrosion resistance of the electrodes in industrial seawater electrolysis plants. While advances in electrode morphology design and surface modifications have improved the longevity of these catalysts, real-world deployment still requires extensive testing under continuous operation conditions [8]. Additionally, direct seawater electrolysis presents technical barriers, such as chlorine evolution and membrane degradation, which must be addressed to ensure cost-competitive hydrogen production [1,2]. The development of stable, corrosion-resistant electrodes that can withstand the harsh conditions of seawater electrolysis is crucial for scaling up this technology.

Recent advancements in single-atom catalysts (SACs) and metal-organic frameworks (MOFs) hold promise for further reducing material costs while enhancing catalytic efficiency and selectivity [4,5]. Moreover, the integration of these catalysts with renewable energy sources, such as offshore wind and solar farms, could improve the economic viability of seawater electrolysis. By reducing dependence on grid electricity, this integration would help lower operational costs and enhance the sustainability of the hydrogen production process [1].

Overall, while nanostructured electrocatalysts have the potential to revolutionize seawater electrolysis and contribute to the production of green hydrogen, their industrial-scale adoption requires further innovation. Continued advancements in sustainable production methods, long-term stability, and cost-reduction strategies are essential to making seawater electrolysis a viable and economically competitive technology for large-scale hydrogen production [9-11].

8.0 FUTURE PERSPECTIVES

8.1 FUTURE RESEARCH DIRECTIONS AND POTENTIAL BREAKTHROUGHS IN NANOSTRUCTURED ELECTROCATALYSTS FOR SEAWATER ELECTROLYSIS

The future of seawater electrolysis is closely tied to the development of highly efficient, stable, and cost-effective nanostructured electrocatalysts that can operate under real-world marine conditions. Several promising research directions are emerging to address current challenges and unlock the full potential of seawater electrolysis for large-scale hydrogen production:

1. Development of Corrosion-Resistant Electrocatalysts

A key challenge in seawater electrolysis is the degradation of catalysts in saline environments. To address this, future research is focused on improving the corrosion resistance of electrocatalysts through the use of metal-organic frameworks (MOFs) and single-atom catalysts (SACs), which show promise for mitigating chloride-induced corrosion [4,5]. Furthermore, the exploration of self-healing materials and protective surface coatings is gaining attention as a means to enhance the longevity of electrocatalysts under harsh conditions [1].

2. Enhancing Selectivity Between Oxygen Evolution Reaction (OER) and Chlorine Evolution Reaction (CER)

The competition between the oxygen evolution reaction (OER) and chlorine evolution reaction (CER) remains a significant obstacle in direct seawater electrolysis. Recent studies suggest that tuning the electronic structure of transition metal-based electrocatalysts, such as NiFe-layered double hydroxides (LDHs) and Co-based catalysts, can improve the selectivity for OER, preventing the formation of harmful chlorine byproducts and enhancing the overall efficiency of the process [2,3].

3. Hybrid and Multi-Component Catalysts

Research is increasingly focused on multi-metallic and heterostructured catalysts that combine metals such as Ni, Mo, Co, and Fe to achieve synergistic effects, improving both catalytic activity and durability [6,7]. The integration of non-metal dopants, such as phosphorus and nitrogen, into these catalysts is also being explored to further enhance their performance, offering new opportunities for highly efficient and durable catalysts in seawater electrolysis [12]

4. Computational Design and AI-Driven Catalyst Discovery

Machine learning and computational modeling are playing an increasingly important role in the discovery and design of new electrocatalyst materials with optimized properties for seawater electrolysis. These advanced approaches enable the rapid screening of potential materials, significantly reducing the trial-and-error process in catalyst synthesis and accelerating the development of novel and highly efficient electrocatalysts [10].

8.2 EXPLORATION OF SYNERGIES WITH OTHER RENEWABLE ENERGY TECHNOLOGIES

The success of seawater electrolysis for sustainable hydrogen production depends not only on advancements in catalyst technology but also on its integration with renewable energy sources and emerging energy storage solutions. Several synergistic approaches are being explored to maximize the potential of seawater electrolysis, with the aim of creating efficient, sustainable, and scalable systems for green hydrogen production.

One such approach is the integration of seawater electrolysis systems with offshore wind farms and floating solar panels, which can form autonomous green hydrogen production hubs. This strategy reduces transmission losses and enhances energy utilization, making it more efficient to produce hydrogen directly from renewable sources [1]. By positioning these systems near renewable energy generation sites, the overall process becomes more cost-effective and energy-efficient.

Efficient storage and utilization of hydrogen produced from seawater electrolysis are critical for its large-scale deployment. Advanced hydrogen storage materials, such as metal hydrides and carbon-based adsorbents, are being explored to improve the energy density and transportability of stored hydrogen, which is essential for its practical application [18]. Moreover, hydrogen fuel cells powered by seawater-derived hydrogen can contribute to the creation of a closed-loop renewable energy system, further enhancing the viability of green hydrogen as a sustainable energy carrier [12].

Another promising avenue is the coupling of seawater electrolysis with CO_2 capture and conversion technologies. This integration enables the simultaneous production of green hydrogen and valuable carbon-based fuels, which would support decarbonization efforts in industrial sectors, such as chemical production and transportation [18,9]. This approach has the potential to significantly reduce carbon emissions while generating renewable energy.

Additionally, future research is exploring the use of alternative feedstocks, such as industrial wastewater and desalination brine, for hydrogen production. By utilizing waste streams for clean energy generation, this method could help mitigate freshwater scarcity while providing a sustainable source of hydrogen production [20]. This concept offers a dual benefit: addressing the challenges of wastewater disposal and enhancing the sustainability of hydrogen production.

9.0 AUTHORS CONTRIBUTION

M.A.D. Aziz (Writing - original draft, Visualization)

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A. Junaidi (Writing – review & editing)

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M.K. Kamarulzaman (Supervision; Resources)

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