

The effectiveness of seawater water splitting for hydrogen production: A review

REVIEW

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Abstract

Hydrogen is a promising fuel due to its high gravimetric energy density. Consequently, hydrogen has become a major research focus not only because of its energy potential, but also its use as a fuel which produces no carbon emissions. However, most current hydrogen production methods still rely on carbon intensive processes, such as methane steam reforming or other fossil fuel-based routes. Hydrogen is therefore commonly classified by color according to the associated carbon emissions, environmental impact and overall cleanliness of the production pathway. As a result, substantial research efforts are currently dedicated toward developing production from non-fossil fuel sources. Seawater, as an abundant resource, offers a promising alternative for hydrogen production through photo-and electro catalysis with the potential for near zero carbon emissions. In this mini review, key parameters affecting seawater electro catalysis, underlying process kinetics, and the various catalyst materials applied for seawater splitting are analyzed.

Keywords: Seawater splitting, chlorine evolution, oxygen evolution, hydrogen evolution.

1. Introduction

The current level of CO₂ emission, at approximately 37 Gt per year and driven by energy production, industrial activities, and the increasing number of automobiles, highlights the urgent need for the development and deployment of net zero technologies [1] [2]. The huge CO₂ emission persists because the world still heavily relies on fossil fuels to meet its energy needs [3]. Hydrogen is considered a promising energy carrier because it can be used to generate electricity without harmful by-products [4]. However, the production

of clean hydrogen remains a challenge [5]. According to IRENA, only about 1% of hydrogen produced around the world can currently be classified as green hydrogen [6]. Therefore, considerable research effort is dedicated to developing clean hydrogen production pathways, including water electrolysis, extraction from clathrate hydrates, and the exploration of naturally occurring geological hydrogen resources, among others [7] [8]. Water electrolysis is currently considered one of the most promising pathways for clean hydrogen production [9]. However, the scarcity of high-quality water presents a major challenge for its large-scale implementation. This has prompted growing interest in the use of abundant alternative water sources, like seawater, for hydrogen generation [10]. Despite this potential, most water electrolysis technologies remain still in the exploration stage. Electrolysis conducted in an alkaline medium is commonly referred to as alkaline water electrolysis (AE) [11]. In contrast, membrane-based systems employ a polymer electrolyte

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membrane to facilitate ion transport while separating protons (H^+) hydroxyl ions (OH^-) [12]. Another approach involves high temperature steam electrolysis, also known as solid oxide electrolysis [13]. It uses a ceramic solid oxygen-ion conducting electrolyte. Among low temperature electrolysis technologies, AE and Proton Exchange Membrane electrolysis (PEM) are currently the most widely adopted and investigated systems [14]. In these electrolysis technologies, feed water purity plays a critical role in determining system efficiency. However, supplying highly purified water to large-scale electrolysis units represents a significant practical challenge. Consequently, seawater has attracted considerable attention as an excellent abundant alternative feedstock for hydrogen production [15-21].

Seawater contains a wide range of ions, including sodium, chlorine, magnesium, calcium, potassium, strontium, sulphates, bromine, fluorine and boron, present in various concentrations [22]. Seawater Electrolysis (SE) electrolysis is classified into two main approaches: In Direct SE (IDSE) and Direct SE (DSE). In IDSE, seawater is firstly purified, typically by reverse osmosis or electro dialysis. By contrast, DSE uses natural seawater directly, after its pH is adjusted to alkaline conditions. IDSE is relatively expensive as it requires additional pretreatment steps to purify seawater. DSE avoids this extra stage and can help stabilize the system against chlorine attack. However, as the electrolyte in DSE is not purified, several challenges arise, such as pitting corrosion, Chlorine Evolution Reaction (CLER) over Oxygen Evolution Reaction (OER), and the deposition of calcium and magnesium salts, all of which affect cell efficiency. Moreover, the resulting effluent, which contain these residues, may itself become a source of environmental pollution. So, to improve the environmental friendliness of DSE, useful by-products in the effluent, such as hypochlorite and Mg and Ca hydroxides can be recovered. Because effective hydrogen production has been reported when the pH of original seawater is suitably adjusted, DSE technique is more attractive than IDSE.

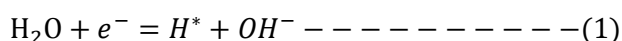
Different DSE studies have employed electrolytes ranging from natural seawater at pH \sim 8.1 to alkaline seawater systems and 0.5 M NaCl solutions used as artificial seawater models. Mcevoy reported the photosynthetic route of water splitting [23]. The development of a graphitic carbon-based catalyst for photo catalytic water splitting was later reported by [24]. Photo catalysis is also considered a promising route for hydrogen production from water resources. For example, many metal (oxy) nitride, metal supplied materials have demonstrated favorable photo catalytic properties [25].

In photo catalytic water splitting, photons are absorbed by a suitable semiconductor photo catalyst. If the photon energy exceeds the band gap of the semiconductor, electrons are excited from the valence band to the conduction band, thereby generating electron-hole (e-h) pairs. These charge carriers are subsequently separated by the inherent electric field gradient inside the material or by fields introduced through doping and structural engineering. The electrons in the conduction band reduce water to generate hydrogen, whereas the holes in the valence band oxidize water to form oxygen. Here, a major challenge is rapid recombination of pairs which limits the overall efficiency of hydrogen production [26]. Combined photo and electro catalysis approaches have also been reported [27]. Graphitic carbon nitride has been reported to exhibit good photo catalytic activity in both acidic and alkaline water. For a material to be an efficient photo catalyst, its band gap should be suitable for utilization of visible light energy, together with suitable band alignment for overall water splitting. The Conduction Band Minimum (CBM) should lie at a more negative potential than the standard electrode potential of H^+/H_2 , and the valence band maximum must be at a more positive potential compared to the standard electrode potential of H_2O/O_2 . Furthermore, the catalyst should support efficient and rapid charge-carrier separation, offer abundant active sites for the redox reactions, and exhibit high stability during operation while scaling up [28]. The efficiency of seawater catalysis for hydrogen production

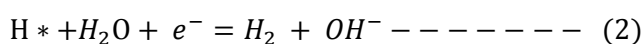
depends on several factors, including reactor design, proton transport, electrolyte pH, operating temperature, catalyst selection, electrode materials, material sustainability, and reactor durability. In all water electrolysis technologies, optimizing of type, structure, composition, configuration, adhesion and stability of the catalyst material is essential for achieving efficient and durable operation [29]. The present review seeks to consolidate the various catalyst materials reported for seawater hydrogen production, including catalysts that facilitate the OER.

2. Fundamental aspects of seawater electrolysis

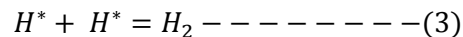
Overall water electrolysis involves two half-cell reactions, one at each electrode. The HER occurs at the cathode and OER takes place at the anode [30]. The full electrochemical cycle is completed by combined operation of HER and OER. As OER follows a four-electron transfer mechanism and requires a higher over potential, it is considered kinetically sluggish and therefore significantly influences the overall efficiency of the whole electrolytic cell. At the cathode, hydrogen evolution can precede either through a Volmer-Tafel or Volmer-Heyrovsky mechanism [31]. Volmer-Tafel route is generally associated with faster kinetic and lower additional voltage requirements compared with the Volmer-Heyrovsky route. In alkaline medium, under an externally applied potential referenced to a standard electrode in a three-electrode configuration, the Volmer reaction can be written as follows:



Heyrovsky reaction corresponds to the electrochemical desorption process, in which an adsorbed hydrogen reacts with a water molecule while simultaneously accepting an electron, leading to the formation of molecular H_2 and an OH^- ion as shown in equation (2).



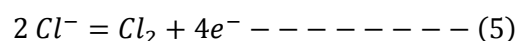
Tafel reaction is faster than Heyrovsky reaction, as it proceeds via the direct recombination of two surfaces-adsorbed hydrogen atoms to generate molecular hydrogen, without the involvement of an additional electron transfer step.



While hydrogen evolution occurs at the cathode, the anode facilitates the OER, as represented in equation (4).

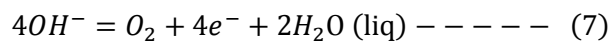
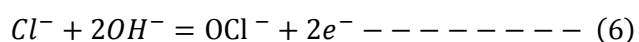


Acidic condition, $E_0 = 1.23 \text{ V vs. RHE}$



Acidic condition, $E_0 = 1.36 \text{ V vs. RHE}$

Under alkaline conditions, where $E_0 = 1.72 \text{ V vs. RHE}$,



$E_0 = 1.23 \text{ V vs RHE}$

These half-reactions occur at the cathode and anode, and their kinetics vary significantly with pH. Hence, the selection of suitable catalysts that can efficiently promote HER and OER at the respective electrodes is critical for enhancing the overall efficiency of water splitting. In seawater splitting, pH plays an especially important role, as catalyst performance is strongly dependent on the pH of the environment. Although platinum is widely regarded as a benchmark catalyst for HER, its reported effectiveness in seawater splitting is limited [32], on carbon, indicating that performance can depend strongly on system configuration and conditions. Splitting remain essential for achieving high efficiency. In addition, the selection and optimization of suitable materials and catalysts must account for the various possible challenges inherent to seawater splitting, including competing reactions, corrosion, and ion-induced fouling, all affecting system performance.

3. Challenges of seawater electrolysis

Although seawater is an abundant resource and can, in principle, be effectively utilized for hydrogen production, its electrolysis faces several unavoidable and significant challenges, as schematically illustrated in (Figure 1). One of the primary issues arises from the high concentration of corrosive chloride ions present in seawater. Chloride-induced corrosion, particularly pitting, poses a serious threat to both electrolyze components and electrode materials. With chloride ions constituting a major fraction of dissolved salts in seawater (≈ 55 wt. % of total dissolved salts), their impact represents a critical limitation in seawater electrolysis systems [33]. Another major challenge is the formation of hypochlorite and other chlorine-containing species during electrolysis, which can lead to catalyst poisoning and reduced system stability. A key issue at the anode is the competition between the Oxygen Evolution Reaction (OER) and the Chlorine Evolution Reaction (CLER). Although in alkaline media the equilibrium potential for chlorine evolution is higher than that for oxygen evolution, thermodynamically favoring OER, the potential difference between the two reactions is relatively small, typically on the order of ~ 400 mV. (Figure 2) Illustrates the potential window under alkaline conditions where OER can be preferentially promoted. However, under practical operating conditions, kinetic factors further complicate this scenario. OER proceeds via a four-electron transfer mechanism and generally requires a higher over potential than CLER. As a result, the effective operational potential window separating OER and CLER can shrink significantly, in some cases to around ~ 200 mV, as reported for IrO_2 -based systems. This narrow window makes it difficult to suppress chlorine evolution while maintaining efficient oxygen evolution. Therefore, an ideal anode catalyst for seawater electrolysis should selectively enhance OER while suppressing or inhibiting CLER [34].

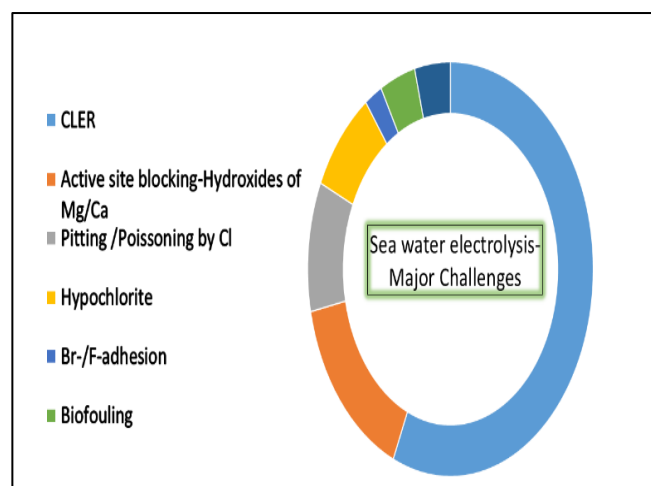


Figure 1: Different challenge factors for effective seawater catalysis

A detailed analysis has provided on the competing potential regimes of OER and CLER, including their representation through Roubaix diagrams have further elucidated mechanistic pathways for oxide-based catalysts, including oxide, metal-peroxide, and Density Functional Theory (DFT)-predicted peroxide pathways, particularly in acidic environments [35]. In alkaline systems, reported efficient non-precious metal nitride catalysts, such as self-supported 3D core-shell NiMoN@NiFeN structures, demonstrating low over potentials of 277 mV for OER and 56 mV for HER at 100 mA cm^{-2} , along with good stability over 100 hours in both KOH-stabilized 0.5 M NaCl and seawater electrolytes and co-workers have comprehensively efficient seawater splitting, with particular emphasis on reaction kinetics [36]. Another significant challenge arises from the precipitation of magnesium and calcium hydroxides under elevated pH conditions. The formation of these hydroxide deposits can obstruct active sites and impede ion transport, thereby hindering the OER. In addition, natural seawater contains various microorganisms and bacteria that can form biofilms on electrode surfaces, leading to the blockage of catalytically active sites and reduced electrochemical performance. Overall, the degradation of seawater electrolysis systems can occur through multiple pathways, including chemical, physical, biological, and mechanical processes.

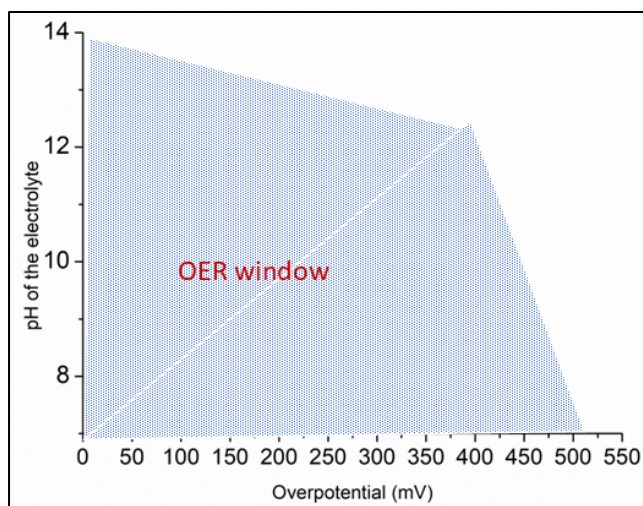


Figure 2: OER potential window under alkaline conditions based on the roubaix diagram

4. Catalysts for seawater catalysis

Direct seawater electrolysis offers a potentially cost-effective approach, as it eliminates the need for purified water. However, in untreated seawater systems, the CLER competes with the OER at the anode due to the narrow thermodynamic potential window between these two processes. Since efficient overall water splitting requires both HER and OER to proceed effectively, the performance of OER becomes particularly critical. Improvements in OER kinetics indirectly enhance HER by maintaining balanced cell operation [37]. Therefore, the design and development of catalysts capable of operating under such adverse kinetic and chemical conditions, while selectively promoting OER over competing side reactions, are essential for achieving efficient and stable seawater electrolysis [38]. Various classes of catalyst materials have been explored to optimize critical electro catalytic parameters, such as reducing over potential, achieving lower Tafel slopes, enhancing long-term stability, and improving resistance to corrosion, while also selectively favoring OER over CLER. Early investigations by Birss and Damjanovic in 1987 on platinum electrodes in alkaline media contributed significantly to the fundamental understanding of OER mechanisms [39]. For the OER, significant research

attention has been directed toward Ni- and Fe-based catalysts, owing to their high activity and cost-effectiveness [40]. In addition, transition metal oxides and hydroxides have been extensively investigated for OER applications [41]. Beyond oxides, alternative catalyst classes such as metal phosphides, sulfides, and nitrides have also been explored for alkaline seawater electrolysis due to their favorable catalytic properties and stability, particularly for enhancing selectivity toward OER and improving resistance against CLER [42]. Furthermore, supports materials, including graphene and carbon-metal hybrid systems, have been reported as effective catalysts and electrode supports in seawater splitting due to their high conductivity and tunable surface properties [43]. More recently, hetero-bimetallic catalysts have gained attention for their synergistic effects, which can significantly enhance catalytic activity and durability in seawater electrolysis systems [44 - 46].

Enhanced performance regarding stability is reported for boron doped Ni/Fe hydroxide for oxygen evolution, exhibiting corrosion resistance for up to 100h [47]. Zhang demonstrated that single platinum atoms supported on MXenes can achieve a remarkably low over potential of approximately 30 mV at 10 mA cm⁻² [48]. Similarly, self-supported Pt/Co combinations are reported exhibiting high electro catalytic surface area (ECSA), indicating strong catalytic performance [49]. Surface modification strategies have also been explored to enhance catalytic activity. Non-precious metal-based catalysts have shown promising results. A dendritic NiCo@NiFe catalyst demonstrated a high current density above 500 mA cm⁻². They have reported Ni/NiFe catalyst systems operating in KOH/seawater electrolytes, achieving over potentials of 209 mV and 222 mV, with corresponding Tafel slopes of 103 mV dec⁻¹ and 156 mV dec⁻¹, respectively. In comparison, a NiCo/NiFe catalyst combination in the same electrolyte system exhibited higher over potentials of 312 mV and 386 mV, but significantly lower Tafel slopes of 46 mV/dec and 57 mV/dec, indicating improved reaction kinetics despite the

higher over potential. MoS₂/Mo₂C composite has been reported to show good electro catalytic parameters [50]. Reported electrolysis in 1 M Phosphate Buffered Saline (PBS) solution with ZIF-65/carbon fabric (CF) varieties.

Among the tested samples, the lowest Tafel slopes achieved were 153.2 mV/dec for HER and 205.7 mV/dec for OER in PBS. In seawater, the corresponding lowest Tafel slopes were reported as 239 mV/dec for HER and 145 mV/dec for OER [51]. They have compared it with the performance of platinum on carbon and IrO₂ in PBS and the sea water with values for Pt/C - 111.6 mV/dec [PBS/HER], IrO₂ - 156.6 mV/dec [PBS/OER], Pt/C - 182.3 mV/dec [Sea water/HER], IrO₂ - 140.7 mV/dec [Sea water/OER] reported a NiFePS-based catalyst that demonstrated an over potential of 216 mV and an overall cell voltage of 1.6 V, maintaining stable operation for 25 hours at a current density of 20 mA cm⁻². Hu et al. 36 developed a self-supported Ni₃Se₂@NiFe Layered Double Hydroxide (LDH) functional catalyst, showing enhanced performance for HER [52]. Furthermore, Chen and co-workers NiFeBa layered double hydroxides for seawater splitting, exhibiting excellent long-term stability of up to 1000 hours lists some of the high current yielding catalyst combinations reported (Table 1). The catalyst material for NiFe LDH, NiCoFe/Bi, NiMoN@NiFeN core-shell, Corrosion resistant Ni/Fe based catalyst. Description Alkaline Sea Splitting for NiFe LDH NiFe-layered double hydroxide nano sheet array intercalated with Benzoate anions RuMoNi FeMoS_x/CoNiP_x

Table 1: OER and overall water splitting performance in alkaline and seawater media

Catalyst Material	Description / Alkaline / seawater splitting	Reference
NiFe LDH	254 mV, 100 mA cm ⁻²	[17]
NiCoFe/Bi	336 mV, 1000 mA cm ⁻²	[53]
NiMoN@NiFeN core-shell	398 mV, 1000 mA cm ⁻²	[15]
Corrosion resistant Ni/Fe based catalyst	Demonstrates prototype-industrial 1 kW scale system, with 73.4 % of energy efficiency at 0.5 mA cm ⁻² at 0.2 V	[18]
NiFe LDH	296 mV, 1000 mA cm ⁻²	[54]
NiFe-layered double hydroxide Nano sheet array intercalated with Benzoate anions	610 mV, 1000 mA cm ⁻²	[55]
RuMoNi	484 mV, 1000 mA cm ⁻²	[56]
FeMoS _x /CoNiP _x	348 mV, 1000 mA cm ⁻²	[57]

HER reaction occurs at the cathode. As discussed in section 2, hydrogen evolution can proceed via either the Volmer-Tafel or Volmer-Heyrovsky pathway [58]. The Volmer-Tafel pathway is kinetically faster route and involves the adsorption of hydrogen ions on active sites, followed by the recombination of two hydrogen ions to form H₂. But, the Volmer-Heyrovsky pathway proceeds via an electrochemical desorption step after adsorption of an hydrogen ion, in which H* at this adsorbed site, reacts with another water molecule and an electron to form H₂, typically resulting in comparatively slower kinetics.

Table 2: High-performance HER catalysts

Catalyst	Description / seawater electrolysis	Reference
Pt/Co/Mo	200 mA cm ⁻² , 194.1mV	[59]
Cu ₃ P/FeP@CC	1000 mA cm ⁻² , 406 mV (0.5)	[60]
Ni/W ₂ N	1500 mA cm ⁻² , 345 mV	[61]
Ir-doped Ni/Fe-based MOF arrays on nickel foam	1000 mA cm ⁻² , 238 mV	[62]
NC/CrN/Ni	1000 mA cm ⁻² , 284 Mv	[13]
NiMoN	1000 mA cm ⁻² , 218 mV	[15]

Platinum is a proven benchmark catalyst for HER due to its optimal hydrogen adsorption energy and its tendency to favor favorable reaction kinetics, often approaching the Volmer-Tafel pathway. However, due to the high cost and scarcity of platinum, significant research efforts have been directed toward the development of non-precious metal catalysts as alternative electrode materials for HER in water splitting systems lists selected high-performance catalyst systems for efficient HER with high current densities (Table 2).

5. Chlorine blocking techniques

Seawater catalysis can be effective and sustainable, if the components which affect adversely on the cell performances are carefully monitored. As chloride attack is most common while dealing with seawater electrolytes, suitable technical improvisation in electrodes and the cell can prevent or reduce the effect of chloride poisoning discusses major three techniques adopted for preventing chloride poisoning. (Figure 3) Introducing protective layers by decorating the electrode surface with specially designed polymer or organic molecules

which can survive against the chloride ions is one of the measures. By inducing repulsive electric force to chloride ions by negative ions including sulphate, carbonate etc. is another technique. The third strategy is to include sacrificial layers, which can selectively adsorb the chloride ions, and this method can protect the active ions sites.

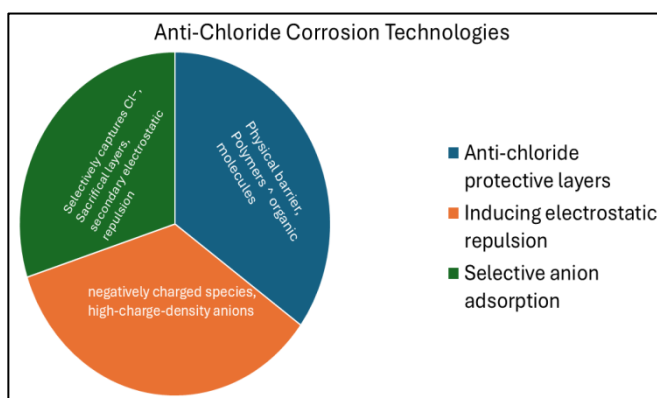


Figure 3: Protective measures against chloride attack in electro catalytic cells

6. Conclusions

Exploring abundant water resources represents a promising alternative to conventional hydrogen production methods. Seawater electrolysis has emerged as an effective route for clean hydrogen generation, with numerous studies reporting high current densities at relatively low over potentials and sustained operation over extended durations. These advancements are increasingly paving the way to industrial applications. With appropriate system design and the implementation of anti-corrosion measures, seawater electrolysis is expected to play a significant role in future clean hydrogen production. This mini review provides an overview of the key kinetic routes of the HER and OER, the requirement and properties of catalyst materials for these reactions, the factors influencing seawater electrolysis, and strategies to mitigate chloride induced corrosion.

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