

Hydrogen Production via Direct Seawater Electrolysis *literature review*

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Contents

AŁ	ostract	
Ac	knowledge	ements4
1	Introduct	ion5
	1.1 Metł	nodology5
2	Overview	of the current literature6
3	Direct sea	water electrolysis 11
	3.1 Hydr	ogen evolution reaction 12
	3.2 Oxyg	en evolution reaction
4	Technical	approaches to the key issues 17
	4.1 Use o	of buffer solutions 17
	4.2 Deve	lopment of catalysts 17
	4.2.1	Hydrogen evolution reaction catalysts 20
	4.2.2	Oxygen evolution reaction catalysts - nickel-based 21
	4.2.3	Oxygen evolution reaction catalysts - cobalt-based 22
	4.2.4	Oxygen evolution reaction catalysts – cobalt and nickel based 23
	4.2.5	Oxygen evolution reaction catalysts - other 23
	4.3 Asym	nmetric electrolyte feed 23
	4.4 Alter	native oxidation reactions
	4.5 Mem	branes for seawater electrolysis 25
	4.5.1	Conventional membranes or diaphragms 25
	4.5.2	Non-conventional membranes 27
	4.6 Mem	braneless electrolysis
	4.7 Solid	oxide seawater electrolysis 32
	4.8 Othe	r water splitting concepts
5	Indirect se	eawater electrolysis
	5.1 Statu	is and deployment of desalination plants
	5.2 Filtra	tion-based desalination technologies
	5.3 Evap	oration/condensation-based desalination technologies
	5.4 Othe	r desalination technologies and integration with external sources of heat

6	Energy demand, cost and land footprint estimates						
	6.1	Energy demand comparison	41				
	6.2	Cost and business case advantages	41				
	6.3	Land use comparison	42				
	6.4	Waste management comparison	44				
7	Con	clusions	45				
8	Reco	ommendations	46				
Re	ferer	nces	48				
Lis	t of a	abbreviations and definitions	57				
Lis	t of f	igures	58				
Lis	ist of tables						

Abstract

Seawater electrolysis is a promising approach for sustainable hydrogen production that could alleviate the ever-growing demand for freshwater resources. This literature review synthesizes current research on direct seawater electrolysis, drawing attention to advances in electrode materials, catalyst efficiency, and system design. Furthermore, an overview of indirect seawater electrolysis is given as a benchmark. Key challenges, including electrode corrosion, chlorine evolution and energy efficiency, are critically analysed. Recent innovations in selective catalysts and membrane technologies are discussed as potential solutions for such challenges. The review also evaluates the economic feasibility of direct seawater electrolysis compared with the established traditional electrolysis using desalinated water. There is currently no research or industrial project demonstrating clear benefits of using direct seawater electrolysis over indirect seawater electrolysis. Our findings, however, do suggest that direct seawater electrolysis can become a viable component of the hydrogen economy for specific target applications.

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Authors

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1 Introduction

In recent years, the water requirement for the production of hydrogen through electrolysis has received increasing attention. The availability of fresh water as feedstock may become a significant hurdle in hot arid regions around the world. These areas may, however, have access to seawater. Seawater is not a suitable direct feedstock for current electrolysis technologies due to the presence of electrochemically active ions that interfere and compete with water-splitting reactions [1]. Therefore, the possibility of direct seawater electrolysis (DSE), without prior water purification (in contrast to indirect seawater electrolysis (ISE) with prior desalination), has been the subject of numerous studies. In Section 2, an overview of publications on this topic is provided.

Compared with ISE, it is expected that DSE could offer the advantage of a smaller spatial footprint and lower energy demand by using a compact device. However, there are numerous challenges to overcome, which are summarised in Section 3; this section also provides a general introduction to DSE. These challenges have been tackled using various approaches. The approaches are introduced in Section 4 and have been organised by their main objective, namely the improvement of catalysts and membranes, the design of membraneless devices and the implementation of alternative reactions. These categories serve as the classification framework for the surveyed literature.

The benchmark for DSE is ISE, which relies on two mature technologies, namely water purification and water electrolysis. An overview of the state of the art of desalination technologies is given in Section 5. Section 6 provides cost, energy demand and land use estimates for ISE compared with DSE. The main conclusions and recommendations can be found in Sections 7 and 8, respectively.

1.1 Methodology

An assessment of available literature focussing on the topic of DSE has been performed. An initial screening on Web of Science using the general prompt 'seawater electrolysis AND hydrogen production' returned 748 papers published between 1992 and April 2024 (for comparison, 15 202 papers dating from 1990 to 2024 were returned using the similar prompt 'water electrolysis' AND 'hydrogen', and 1 512 papers were returned using the prompt 'seawater electrolysis'). Further screening based on specific terms, including 'catalysts' and 'membranes', or other subcomponents was performed but did not return meaningful results at this stage.

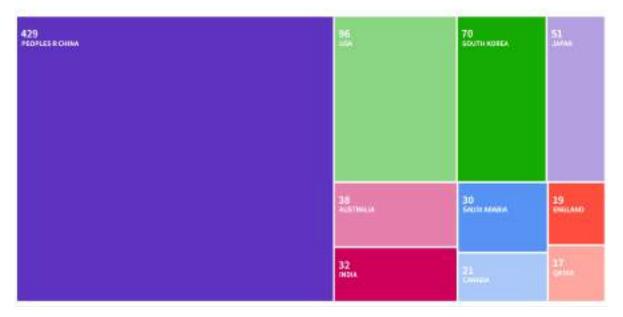
In addition to this initial Web of Science screening, further research based on the review papers obtained from the screening led to the addition of 20 more papers. From the 768 total papers, 66 were selected for further analysis. Additional relevant papers were identified through targeted searches focused on specific topics, such as solid oxide DSE. The final selection was a combination of the most cited papers (31 papers with more than 100 citations) and other papers identified as being representative of various technical approaches. The general trends obtained from this analysis are detailed in Section 2 which examines the countries of origin, an assessment of the most important research focuses of the papers, the scale of the projects detailed therein and the types of water used in the experiments.

This analysis serves as a basis for Sections 3 and 4, which provide more details on the most important issues, as well as the technical approaches that have been most recently investigated by the research community on DSE.

2 Overview of the current literature

Based on the countries of origin of the papers, China seems to dominate the research activities related to seawater electrolysis for hydrogen production, with 429 papers, followed by the United States (96 papers), South Korea (70 papers) and Japan (51 papers). The breakdown by country of authorship is illustrated in **Figure 1** and the institution involved are shown in **Figure 2**.

Figure 1 Top 10 countres of origin of the authors of the papers identified by the Web of Science prompt 'seawater electrolysis AND hydrogen production'.



Source: Web of Science¹ (July 2024).

Figure 2 shows the most common institutional affiliations of the papers' authors. No industrial entity counts among the top 10 affiliations; most affiliated institution overall are universities.

¹ https://www.webofscience.com

Figure 2 Institution of origin of the papers identified by the Web of Science prompt



Source: Web of Science data.

Out of the total papers, 722 acknowledged receiving mainly public funding, of which 184 were supported by the National Natural Science Foundation of China. The ZiQoo Chemical Co. Ltd. of Japan partially supported six publications, but, otherwise, mention of industrial partners was rare.

The number of publications exponentially increased after 2020, as illustrated in **Figure 3**, with more than 250 publications in 2023. In 2024 (data available until July), the share of papers with affiliations in the EU 27, Norway, Switzerland and the United Kingdom seemed to be increasing.

Research intensity on DSE is much lower in the EU than in Asia (particularly China) and other regions, with no EU Member State appearing in the top 10 countries of origin of the reviewed papers, as shown in Figure 1. Key players in this field in Europe seem to be the Technical University of Berlin (Germany), with five publications (two of which are reviews) in the 66 selected, and the University of Leiden (Netherlands) with one. In terms of EU-funded projects on seawater electrolysis, there is one on-going project funded through the European Innovation Council, ANEMEL [4] (EIC, 2022-2026). It focuses on creating an anion exchange membrane (AEM) electrolyser using low-grade water sources like saline and wastewater to produce hydrogen from renewable energy sources. The project plans to achieve this by developing selective and efficient membrane-electrode assemblies (MEAs) with non-critical raw materials as electrocatalysts and membranes without fluorinated compounds. The objective is to develop an AEM device that operates at low overpotentials, requires minimal water pretreatment and operates at a current density above 1 A/cm². No papers have been published yet by the partners of the project.

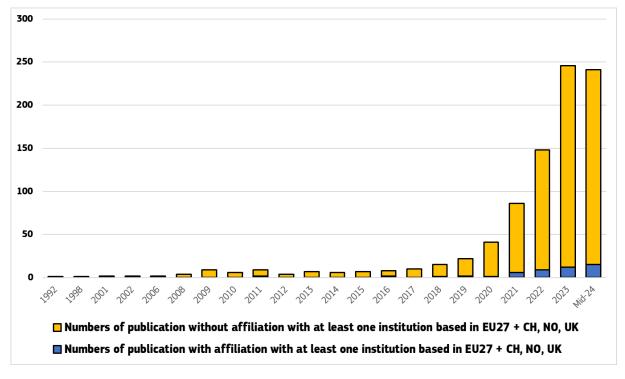
There are no other ongoing European projects on seawater electrolysis to our knowledge, but at least one more is likely to start in 2025. The recent Clean Hydrogen Joint Undertaking call topic HORIZON-JTI-CLEANH2-2024-01-03 had the following objectives:

- energy consumption at nominal load: 53 kWh_e/kg for low-temperature electrolysis and <40 kWh_e/kg + <10 kWh_{th}/kg for high-temperature electrolysis;
- current density for nominal operation: ≥ 0.5 A/cm²;

- degradation: $\leq 5\%/500h$;
- operational flexibility: 20 % to 100% of nominal load;
- minimal capacity of the electrolyser: 20 gH₂/h;
- platinum-group metal (PGM) electrode load: < 0.4 mg/W;
- achieved purity of hydrogen: at least 99 %;

The indicative budget of the call is EUR 4 million. The call has received 23 proposals, showing that, in spite of a comparatively low publication rate in Europe, there is high interest in this topic. One project has been selected for funding, and seven are on the reserve list²

Figure 3 Number published per year, between 1992 and mid 2024, of the papers identified by the Web of Science prompt, and affiliation of authors.



Source: Based on Web of Science data.

As described in the introduction, 66 out of the 768 papers were selected for further analysis. Of these papers, 19 were classified as reviews. The studies performed in the remaining 47 papers addressed at least 1 of the 12 identified main research topics. A short overview of these 47 papers is provided in this study. **Figure 4** shows the number of papers covering each of these 12 research

² https://www.clean-hydrogen.europa.eu/system/files/2024-08/Call%20Update%202024%20-%20Flash%20Evaluation%20Results.pdf

focuses, taking into consideration that almost all of the papers cover more than one topic. We have identified these topics by assessing and grouping the reviewed papers.

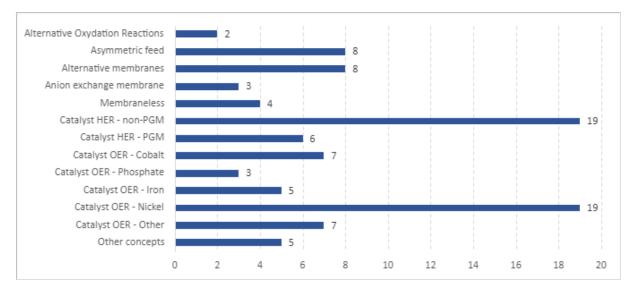


Figure 4 Number of papers tackling the 12 identified research focuses. HER, hydrogen evolution reaction; OER, oxygen evolution reaction.

Source: Based on Web of Science data.

The surveyed literature generally focuses on advancing low-grade seawater electrolysis to enhance efficiency and long-term durability, but various approaches are taken. According to He et al. [2], one common approach involves optimising catalyst/electrode materials and adjusting the reaction environment by means of controlled electrochemical selectivity to tackle the primary catalytic challenges of anode chlorine chemistry. Another approach concentrates on removing impurities and ions using pre-treatment or integrated separation methods to mitigate the adverse effects of seawater on commercial electrolysers. Alternative oxidation reactions and coupling of electrolysis with reverse electrodialysis (RED) have also been explored. It is worth noting that there is no clear terminology for DSE. In this report we consider technologies that use a combination of water purification and electrolysis processes in the same device to be DSE. In some papers this approach has been referred to as hybrid DSE.

The quantitative assessment in **Figure 4** Number of papers tackling the 12 identified research focuses shows that research activities mainly focus on a particular type of approach: the development and performance analysis of catalysts. On the anode side (oxygen evolution reaction (OER)), several types of catalysts were investigated, with a clear focus on nickel-based catalysts. On the cathode side (hydrogen evolution reaction (HER)), the assessment shows a higher level of interest in the development of non-PGM catalysts. The results of this analysis are detailed in Section 3 of this report.

Much of the research on seawater electrolysis is performed in simple two- or three-electrode reactors without any membrane, which can help us to understand the catalytic reactions at a fundamental level. Out of the 47 papers reviewed, 19 used a membrane in their experimental setup. The transfer of these results to device-scale applications or even to the MEA level has not often been attempted [3]. Regarding membranes, AEM were most commonly used, with few exceptions (see Sections 4.5.1.2 and 4.5.2). Several researchers have tried to implement DSE at high temperatures in solid-oxide-based cells (see Section 4.7).

Most commonly, the electrolyte chosen was alkaline seawater (in 26 papers), using water collected from nearby beaches and filtered to remove visible impurities. Typically no further analysis of the seawater was made to investigate the quality and quantity of impurities. The remaining papers used synthetic seawater, through the addition of salts to water.

As for the alternative approach employing the pre-purification of seawater, several researchers used different types of membranes to exclude salt ions (see Section 4.5.2).

In the papers investigated, there was a lack of research in terms of sustainability impacts or safety. Specifically, there is not much information regarding the waste products of the DSE process, such as brine or diverse precipitates.

3 Direct seawater electrolysis

DSE is being investigated as a solution to the issue of the availability of freshwater.

Proton exchange membrane (PEM) and alkaline water electrolysis (AWE) need ultra-pure water (UPW), which is typically characterised by high resistivity (measured in Ω /cm). There are two standards used to specify water purity for electrolysis. The US-based ASTM International (code D1193-06(2018)) and the ISO 3696(1987) identify several grades of water purity. Often manufacturers will request a supply of Type 2 water as a minimum purity, with a minimum resistivity of 1M Ω /cm. For PEM electrolysis, Type 1 water with a resistivity of > 18 M Ω /cm might even be preferred, which, according to the ASTM standard corresponds to a maximum content of 1 µg/l of both sodium and chloride [5]. In addition to the resistivity, the total organic content and total silica are specified in the standards for electrolysis feedwater. AWE water purity is not often discussed in the literature, but at least Type 2 water is likely to be a requirement [6]. As seawater has a much lower resistivity than UPW (around 30 Ω /cm [7]) and contains ions and other species well above the thresholds given in the standards for UPW, detrimental effects on the electrolyser are expected when using seawater.

Water electrolysis is performed by means of two reactions, the HER at the cathode and the OER at the anode (e.g. [8]). The reactions depend on the acidity or alkalinity of the water.

In acidic conditions:

Cathode: HER: $2H^+ + 2e^- \rightarrow H_2$ (g)

Anode: OER: $2H_2O(I) \rightarrow 4H^+ + O_2(g) + 4e^-$

In alkaline conditions, and near-neutral conditions:

Cathode: HER: $2H_2O(I) + 2e^- \rightarrow H_2(g) + 2OH^-$

Anode: OER: $4OH^{-} \rightarrow O_2$ (g) + $2H_2O$ (l) + $4e^{-}$

One important aspect of using seawater for electrolysis is that seawater is not homogeneous and its composition varies based on geography and season. Seawater, therefore, can present itself at different pH levels from acidic to alkaline, with an average pH of 8.1 [9].

Most of the research activities on DSE are currently performed at the laboratory level, and no commercial plant using DSE has been deployed to the best of our knowledge. Significant technical challenges remain to be solved before direct seawater-splitting technologies can be scaled up. An essential objective for seawater electrolysers is developing robust, selective electrodes/catalysts to minimise undesired electrochemical processes, particularly chloride reactions. Active and selective catalysts have been identified (see Section 4.2), but advanced membranes and separator concepts are also crucial for increasing the stability of electrolysers (see Sections 4.5-4.8).

The main challenges arising from the use of a seawater feed for water electrolysis stem from the level of natural impurities found in seawater, from organic matter to ions [10]. Impurities such as sediments and microorganisms can be addressed with pretreatment methods. However, numerous ions, for example chloride (Cl⁻), sulphate (SO₄²⁻), sodium (Na⁺), magnesium (Mg²⁺), calcium (Ca²⁺), bicarbonate (HCO₃⁻), and carbonate (CO₃²⁻) are present in seawater and cannot be easily removed through filtration. These ions can affect the electrolysis process at different levels based on the electrolyser design, causing formation of precipitates on the electrodes, corrosion of electrodes,

membrane degradation and in general reducing electrolyser efficiency (see Table 1 Average concentration of impurities in seawater with around 3.5% salinity and their reactions during DSE. . Despite regional variations in seawater composition, the average salt concentration is around 3.5 wt%, primarily consisting of Na⁺ and Cl⁻ ions [1].

The main problems faced by DSE can be summarised as the following:

- the presence of ions in seawater (see **Table 1**), which leads to corrosion and a loss of performance and durability of the catalysts and the membrane;
- competition between the OER and chloride reactions at the anode;
- change in the pH at the electrodes, which can cause precipitation of impurities and degradation of the electrodes;
- low current densities.

Ions and Gases	Concentration (ppm)	Reaction during electrolysis
Cl	19,400	OER competitive chlorine evolution reaction (CER) includes OCl^- (Hypochlorite ion), HOCl (Hypochlorous acid) and Cl_2 (chlorine) production.
Na ⁺	10,800	(hypochlorite NaOCl) formation in the presence of chlorine.
SO ₄ ²⁻	2700	Insoluble sulfate minerals (MgSO ₄ , CaSO ₄ etc.) production
Mg^{2+}	1300	Insoluble precipitate $Mg(OH)_2$ production under alkaline condition
Ca^{2+}	400	Insoluble precipitate Ca(OH) ₂ production under alkaline condition
K^+ , HCO_3^- , Br^- , B	400, 100,70, 30,	Unavoidable Parallel reactions
(OH) ₃ /B(OH) ₄ , CO ₃ ²⁻ , Sr ²⁺ , F ⁻	10, 10, 1	
Other inorganic impurities	0.6	Unavoidable poisoning effect
Organic impurities	1–2	Unavoidable poisoning effect
Gases, Ex. N ₂ , O ₂ , Ar	19	Gas crossover and local pH modification

Table 1 Average concentration of impurities in seawater with around 3.5% salinity and their reactions duringDSE. CER, chlorine evolution reaction; ppm, parts per million.

Source: Mishra et al. [11] © 2023 Elsevier Ltd. All rights reserved.

3.1 Hydrogen evolution reaction

The primary challenge at the cathode is the potential obstruction of the electrocatalyst active sites, as shown in **Figure 5**.

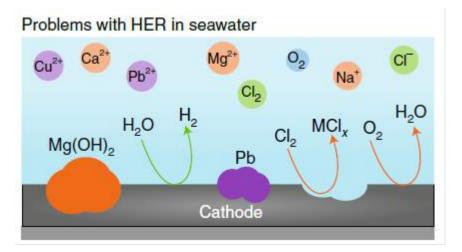
The chlorine and oxygen corrosion is mostly a challenge for the anode; however, it could affect the cathode following gas crossover. In addition, the oxygen crossover at the cathode can result in

oxygen reduction reactions, diverting electrons from the HER, which decreases overall efficiency. This process also leads to the degradation of the cathode over time [11]. To address these issues, the use of electrocatalyst corrosion-resistant materials, such as nickel-iron (Ni-Fe) or nickel-cobalt (Ni-Co) alloys, is recommended [12]. In addition, separation membranes between electrodes need to be tailored to the specific electrolyser design in order to reduce gas crossover.

As the electrolysis current increases, the local pH near the cathode surface experiences a substantial rise, potentially resulting in the formation of precipitates, such as calcium hydroxide $(Ca(OH)_2)$ and magnesium hydroxide $(Mg(OH)_2)$, from cations in the seawater that deposit on the electrode surface. This reduces the number of active sites for HER and the lifespan of the cathode.

In order to be able to perform DSE in the long term, the issue of severe pH fluctuations must be addressed. Currently, the main solution is to incorporate a pH buffer (e.g. a potassium hydroxide (KOH) solution) into the seawater electrolysis system to stabilise pH changes (e.g. [8]). Furthermore, catalysts able to regenerate themselves and remove the deposit of precipitates are being developed. Alternatively, the use of additional purification strategies for the electrolyte or new electrolyser designs and membrane applications are being studied and implemented to avoid the presence of impurities in contact with the electrode.

Figure 5 Graphic representation of possible issues at the cathode for HER in seawater. The green arrow is the HER, orange arrows are corrosion reactions and Mg(OH)₂ as well as Pb represent possible depositions of impurities (oxides or metallic).



Source: Adapted from Tong et al. [12], © 2020, Springer Nature Limited. All rights reserved.

3.2 Oxygen evolution reaction

At the anode, the main challenge is the production of corrosive compounds, especially when increasing the current density.

The presence of chloride ions in seawater enables the chlorine evolution reaction (CER), or the formation of hypochlorous acid, HClO, and hypochlorite, ClO⁻. An early study conducted in 1980 [13] showed that, at reasonable current densities, CER dominates, while the desired OER is favoured only at low current densities.

Chlorine gas generated during CER can oxidise and contaminate metal parts in the catalysts and other components, causing suboptimal efficiency and stability. Similarly to chlorine, the formation of hypochlorite is dangerous to health, the environment and electrolyser durability. Furthermore, these species reduce the purity of the oxygen emitted, requiring the addition of a gas-filtering system. While Cl₂, HCIO and CIO⁻ are commercially used chemicals, they are not considered valuable co-products [14]. Chlorine is difficult to transport and therefore is usually generated on the site of the chemical process where it is used [15].

Avoiding these reactions is technically challenging mainly because these competitive reactions are kinetically faster than the OER due to the lower number of electrons involved [16] (two electrons for the chlorides and four electrons for the OER). As depicted in the Pourbaix diagram (**Figure 6**), the chloride reaction pathways require different conditions based on pH.

In acidic conditions:

CER: $2Cl^2 \rightarrow Cl_2 + 2e^-$

At pH 3-7.5:

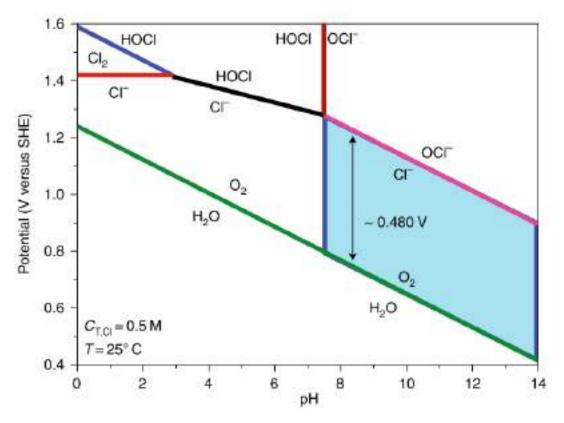
Hypochlorous acid formation: $Cl^- + H_2O \rightarrow HClO + H^+ + 2e^-$

In alkaline conditions:

Hypochlorite formation: $Cl^{-} + 2OH^{-} \rightarrow ClO^{-} + H_2O(l) + 2e^{-}$

The potential of hypochlorite formation depends on pH value, while the potential of chlorine generation is independent of the pH. The OER holds a slightly more favourable thermodynamic profile than the CER across the pH range, with the potential difference expanding as the pH increases to the values of hypochlorous acid and hypochlorite formation reactions. At a pH > 7.5, the potential difference reaches a maximum value of approximately 480 mV.

Figure 6 The Pourbaix diagram as elaborated by Dionigi et al. [15], from [12], the potential is calculated against a standard hydrogen electrode (SHE). The green line represents the thermodynamic equilibrium between water and oxygen. At electrode potentials higher than the green line, the OER process becomes thermodynamically possible. The red line shows the competing acidic oxidation of chloride to free gaseous chlorine. The black and pink lines mark the onset of the oxidation of chloride to hypochlorous acid, HClO, or hypochlorite, ClO⁻. The potential difference between the chloride chemistry and the water oxidation is the highest at 480 mV in alkaline media at a pH > 7.5 (light blue region), where chloride is oxidised to ClO⁻ [12].



Source: Tong et al. [12], © 2020, Springer Nature Limited. All rights reserved.

This means that, under alkaline conditions (pH > 7.5), an OER catalyst can exhibit a maximum overpotential of up to 480 mV without any interference from chloride chemistry. This provides a guideline for designing and operating systems to minimise unwanted side reactions, as originally proposed by Dionigi et al. [15]. In acidic conditions, the potential difference between CER and OER is smaller, making it considerably more challenging to achieve high currents at electrode potential. In an acidic environment with a pH of 0, the theoretical overpotential of the OER is 130 mV lower than that of the CER.

Consequently, alkaline conditions appear more favourable for seawater splitting, which is evidenced by the large number of studies following this approach (27 out of 47 papers, with another 3 using mixed acidic-alkaline electrolytes).

One of the means of suppressing the CER is by keeping the overpotential of the OER below 480 mV. However, such a low overpotential limits the maximum current density in the electrolytic cell to values much lower than those found in commercial systems. In the reviewed literature, the current density reported for DSE was generally below 200 mA/cm², which is considerably lower than the industrial alkaline standard (600 mA/cm²) [17].

Most research focuses not on using natural seawater directly as an electrolyte but rather on adding buffers³ such as KOH to increase alkalinity. This approach is necessary because high current densities can lead to a pH decrease at the anode [1]. Similar to the challenges at the cathode, as described in Section 3.1, significant pH changes near the electrode surface during electrolysis can result in salt precipitation, catalyst degradation and electrode degradation. This is further described in Section 4.1.

³ A buffer is a chemical solution used to stabilise (buffer) the pH variation in a solution.

4 Technical approaches to the key issues

4.1 Use of buffer solutions

Seawater, without any additives, can theoretically be employed for water splitting. However, the concentration of ions in seawater is low, leading to low conductivity and low efficiency [18]. In addition, local pH variations at the electrodes negatively influence the thermodynamics of the hydrogen and oxygen evolution half-reactions and may also result in the precipitation of various species, such as alkaline earth hydroxides. Several researchers have designed systems that introduce a buffer, either base or acid, to mitigate the pH changes and address low conductivity [19], for an overview, see **Table 2**. In traditional electrolysis, when high-purity water is employed, the buffer solution can persist for an extended duration within the electrolyser. This is because only H₂O is depleted during electrolysis, and it is therefore sufficient to merely supplement the inexpensive high-purity water without additional substances [20]. On the other hand, in DSE, the buffer solution is consumed due to reactions and the precipitation of the ions present in seawater, and it needs to be replenished periodically, leading to additional costs.

Most research on DSE has been conducted using alkaline buffer solutions based on 1 M KOH solutions. As mentioned in Section 3.2, alkaline conditions are advantageous to avoid the CER. Furthermore, a KOH solution is used in excess in order to further purify seawater and trigger the precipitation of ions such as Mg^{2+} and Ca^{2+} and avoid their deposition on the electrodes [21]. On the other hand, alkaline conditions reduce the HER kinetics [22], due to the bottleneck at the Volmer step⁴ [23], increasing the need for catalysts able to work at high pH conditions [24] this also make it difficult to use traditional electrolysers such as PEM electrolysers (PEMELs).

4.2 Development of catalysts

To improve the efficiency of hydrogen production, catalysts are used on the electrodes of the electrolyser. The catalysts must be highly active for the HER and the OER to improve their kinetics and efficiency. To overcome some of the challenges mentioned in Sections 3.1-3.2, catalysts should be able to selectively block competitive reactions such as CER, and they should resist corrosive environments.

For the HER, common catalysts that are able to work across a large range of pH values include the following:

- PGMs like platinum (Pt) and ruthenium (Ru) are highly effective but also scarce and have low durability. Therefore, they are not often used in DSE research unless with mixed compounds [25].
- Non-noble metal catalysts, such as cobalt-molybdenum (NiMo) alloys, can offer good catalytic activity and stability at a lower cost.

⁴ water dissociation and adsorbed hydroxyl desorption

For the OER, as mentioned before, catalysts need to resist chloride corrosion and prevent the formation of chlorine gas or hypochlorite:

- nickel-iron (Ni-Fe) oxides and Ni-Fe layered double hydroxides (LDHs) have shown promising activity and stability;
- (Co)-based catalysts⁵ are also being studied for their cost-effectiveness.

Much attention has been paid to the development of efficient and selective OER electrocatalysts with high OER kinetics, low CER kinetics and good corrosion resistance at alkaline conditions [26].

Regarding the development of new catalysts, interest is growing in the design of self-supported electrocatalysts [27]. Traditional powdered catalysts require the addition of binders to coat the electrode substrate, with the consequence of covering many active sites and reducing overall performance. Furthermore, while research on HER catalysts is centred on materials able to work at different pH values, OER catalyst development is focused on neutral-alkaline media, due to the poor efficiency at low pH values caused by the competition of the CER reaction [27]. Worth mentioning is the approach of Vos et al. [28], using manganese oxide, which showed improvement of the OER selectivity in acidic media. However, the results showed that the improved OER was not dependent on the catalytic activity of the MnO_x but rather because of the barrier effect that was generated, reducing the impact of the CER. In Table 2, an overview of the catalysts used for the different electrodes in the reviewed papers is given.

In the following paragraphs, we will address the catalysts used in the reviewed papers. In Section 0 we will mention the papers that investigated the catalysts affecting only the HER reaction. In the subsequent Sections 4.2.2-4.2.5, we will review those catalysts affecting only the OER and the catalysts that were developed as bifunctional catalysts, but for which the focus on the OER is predominant. The paragraphs discusing the OER are further distinguished based on the main catalyst material. For most of these studies, the experiments were performed on simple devices consisting of two or three electrodes and without membranes, the few exceptions are mentioned in Table 2.

Table 2 Overview of the papers reviewed focusing on catalyst materials, tested in seawater. Buffer solutions were used to change the electrolyte pH. Usually the experiments were carried in a two- or three- electrodes cell; when specified a membrane was also used. AEM, anion exchange membrane; NF, nickel foam; OEC, oxygen evolution catalyst; PBS, phosphate-buffered saline solution; SA, single atom.

Authors	Catalyst composition	Reaction	Electrolyte	Testing duration (hours)	Membrane	Buffer solution
Dresp, S et al. [3]	NiFe	HER	Alkaline simulated seawater	100	AEM	-
Li, DY et al. [29]	Co ₂ P-Ni ₂ P	HER	Acidic to alkaline simulated seawater	-	-	1 M H ₂ SO ₄ / 1 M PBS / 1 M KOH

⁵ Cobalt is considered a critical raw material in the EU according to the Critical Raw Materials Act https://eurlex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32024R1252

	CoMoP@C <u>(ª)</u>	HER	Natural	10	-	-
[30]			seawater (no specified pH)			
Wu, LB et al.	Ni-MoN	HER	Alkaline	100	AEM	1 М КОН
[31]			seawater			_
Wu, XH et al.	Co _x Mo _{2-x} C/MX	HER	Acidic to	225	-	-
[32]	ene(^b)/NC		alkaline			
			seawater			
Yang, F et al.	Pt/Ni-Mo	HER	Alkaline	24	Alkaline	1 M KOH
[33]			simulated		membrane	
			seawater			
Yu, L et al. [34]	NiCoN /Ni _x P	HER	Natural	24	-	-
			seawater (no			
			specified pH)			
	Ni-SA/NC	HER	Neutral to	14	-	1 M KOH
[35]			alkaline			
			seawater			
	MnO _x IrO _x	OER	Acidic saline		-	-
[28]			water			
Guo, JX et al.	CoO_x - Cr_2O_3	OER	Neutral	100	Nafion	-
[36]			seawater			
Kuang, Y et al.	NiFe/NiS _x /NF	OER	Alkaline	1000	-	1 M KOH
[37]			seawater			
	Ni₃S₂@NiFePB	OER	Alkaline	225	-	1 M KOH
	A/NF		seawater			
.	Na ₂ Co ₁₋	OER	Alkaline	100	Alkaline	0.1 M
	_x Fe _x P ₂ O ₇ /C		seawater		membrane	КОН
•	B-Co ₂ Fe	OER	Alkaline	100	-	1 M KOH
	LDH/NF		seawater			
•	Fe,P-NiSe ₂ -NF	Bi-	Neutral to	200	AEM	0.5 M
[41]		functional				КОН
			seawater			
-	NiFeS/NF	Bi-	Alkaline	50	-	1 M KOH
[42]	0.050	functional	seawater			
,	Co-OEC	Bi-	Neutral to		-	1 M KOH
al. [43]		functional	alkaline			/ 1 M KPi
Cae Vietal	Kenet/() NE	D:	seawater	24		/ 1 M KBi
	Karst(^c) NF	Bi- functional	Neutral	24	-	-
[44]		functional	seawater			
Wang, SH et al.	Co-Fe₂P/NF	Bi-	Alkaline	22	-	1 M KOH
[45]		functional	simulated	~~		
[]		. directorial	seawater			
Wu, DL et al.	Ru-CoO _x /NF	Bi-	Alkaline	100	-	1 M KOH
		functional	seawater			
[46]			Alkaline	48	AEM	1 M KOH
[46] Wu. LB et al.	Ni ₂ P-Fe ₂ P	BI-	Aikaiiie	40		
Wu, LB et al.	Ni ₂ P-Fe ₂ P	Bi- functional		40		
Wu, LB et al. [47]	Ni ₂ P-Fe ₂ P S-(Ni,Fe)OOH	BI- functional Bi-	seawater	100	-	1 М КОН

Yu, L et al. [49]	NiFeN- NiMoN/NF	Bi- functional	Alkaline seawater	100	-	1 M KOH
Zhao, Y et al. [50]	NiNS	Bi- functional	Neutral seawater	12	-	1 M KOH
Zhao, YQ et al. [51]	CoSe	Bi- functional	Neutral seawater	12	-	1 M KOH

(a) Cobalt molybdenum phosphide nanocrystal coated by a few-layer N-doped carbon shell.

(^b) MXenes are two-dimensional materials, where M represents an early transition metal such as titanium, vanadium or molybdenum and X is a carbon and/or a nitrogen.

(^c) Topography of the nickel foam.

4.2.1 Hydrogen evolution reaction catalysts

As mentioned in Section 3.1, the main goal of catalysts at the cathode is not to avoid competing reactions but rather to increase the HER kinetics while being able to withstand corrosion and the deposition of impurities on active sites. For example, an electrocatalyst designed with high hydrogenbubble release could prevent the effects of impurities by flushing them out [10].

Currently, platinum-based nanostructured catalysts are the most active materials for the HER, but their scalability is limited by their high cost due to the scarcity of the necessary materials [52], [53]. Furthermore, they show high activity mostly in acidic electrolytes, which are avoided for an optimal OER [54]. To address the precursor material use, Yang et al [33] reported the development of electrocatalysts with highly dispersed PGM nanoparticles. A Pt/Ni-Mo catalyst showed a low overpotential of 113 mV at 2 A/cm² operating in saline-alkaline water (1 M KOH and 0.5 M NaCl).

Alternatively, bifunctional catalysts are of high interest. They provide an interesting solution in order to develop electrolysers that can switch anode and cathode periodically, allowing for electrode regeneration [12]. However, for these catalysts, the literature focuses more on the OER performance, which will be discussed in the following sections (4.2.2-4.2.5).

Dresp et al. [3] showed that the performance of a NiFe hydroxide catalyst for the cathode in alkaline seawater increased with higher concentrations of KOH, but the electrocatalyst exhibited lower stability. Moreover, using a working-resting cycle instead of a continuous operation of the electrolyser showed a recovery effect on catalyst performance during the resting time. A low OER selectivity was registered, with a faradaic efficiency of 88% at high current densities (3 A/cm²). Wu et al. [31] developed a Ni-MoN catalyst, that showed stability in seawater + 1 M KOH for over 110 hours at a current density of 500 mA/cm². Yu et al. [34] combined Ni_xP foam with NiCoN nanoparticles as a catalyst with high conductivity and corrosion resistance in addition to a three-dimensional structure with a large surface area.

Li et al. [29] developed an electrocatalyst by connecting Co_2P and Ni_2P nanoparticles together, resulting in a nanoporous structure. This showed an HER overpotential of 46 mV at 20 mA/cm² in a range of pH from acidic to alkaline. Ma et al. [30] developed a catalyst using cobalt and molybdenum phosphide nanocrystals, coated on N-doped carbon (CoMoP@C). Tested in seawater, it showed stability for 10 hours and a faradaic efficiency of 93%. On the other hand, working with multiple pH levels, Wu et al. [32] developed a $Co_xMo_{2-x}C/MXene/NC$ catalyst with high faradaic efficiency (98%) and durability for over 225 hours in seawater. The study showed an overpotential of 500 mV at 45, 30 and 15 mA/cm², respectively, for loadings of 0.6, 0.4 and 0.2 mg/cm² of the catalyst. A systematic examination of single atom catalysts⁶ was carried out by Zang et al. [35], albeit at low current densities. The authors reported nickel single-atom electrocatalysts exhibiting HER overpotentials of 102 and 139 mV at 10 mA/cm² in fresh water and seawater, respectively, and found that nickel atoms in a triple nitrogen coordination enhanced HER.

4.2.2 Oxygen evolution reaction catalysts - nickel-based

As mentioned in Section 3.2, Dionigi et al. [15] stated that alkaline conditions are preferable for obtaining high selectivity for the OER. Catalysts should be able to sustain an operating current with an overpotential of < 480 mV, in order to achieve oxygen/hydrogen selectivity. In Dionigi et al.'s 2016 paper, they found that NiFe-LDH satisfies this condition at pH 13 in a seawater-mimicking electrolyte. Tests were performed at a current density of 10 mA/cm² [15]. Only short-duration tests of two hours were performed.

Zhao et al. [50] developed a nickel nitride/sulphide electrode (NiNS) as a bifunctional electrode. In short duration, laboratory-scale experiments conducted in 2019, it could achieve current densities of 48.3 mA/cm² at 1.8 V in seawater. The electrocatalytic performance of NiNS was attributed to the interface between Ni₃N and Ni₃S₂ [50]. In the same year, Kuang et al. [37] reported experiments with a NiFe/NiS_x/Ni anode. The test was carried out in 1M KOH added to seawater from San Francisco Bay. The electrolyser operated at a current density of 400 mA/cm² under a voltage of 2.12 V continuously for more than 1 000 hours without performance loss [37].

Most of the reports on nickel-based catalyst materials deal with alkaline electrolytes. Gao et al. [44] developed a nickel foam (NF)-based monolithic electrode for both electrocatalytic HER and OER in neutral media. The catalytic performance attributed to the surface Ni/ α -Ni(OH)₂ heterostructure is beneficial for the kinetics of both HER and OER.

Wu et al. [47] proposed a bifunctional Ni₂P-Fe₂P microsheet three-dimensional NF structure that facilitates the release of oxygen bubbles and the diffusion of the electrolyte on the active surface. Tests in seawater with the addition of 1M KOH showed potentials of 1.8 and 2.0 V to drive current densities of 100 and 500 mA/cm², respectively. The catalyst showed good stability over a period of 48 hours without the formation of chlorine species. However, the formation of oxides (Ca, Na, Mg) on the electrode was observed.

Similarly, Yu et al. [48] focused on the morphology of Ni catalysts. Forming nanoparticle layers of the catalyst with multiple levels of porosity provides more exposed active sites and increases the catalyst's efficiency. Furthermore, the porous structure promotes the release of oxygen bubbles, liberating the active sites of the surface. In their work, Yu et al. [48] tested in natural seawater (with the addition of 1M KOH) the S-(Ni,Fe)OOH catalyst, reaching potentials of 1.7, 1.8 and 2 V to drive current densities of 100, 500 and 1000 mA/cm², respectively, achieving nearly 100 % faradaic efficiency and a high OER selectivity over CER. The tested catalyst showed stability for over 100 hours. Chen et al. [42] reported similar results to Yu et al. [48] for a bifunctional NiFeS catalyst built on an NF structure. It reached potentials of 1.7 and 1.9 V to drive current densities of 100 and 500 mA/cm², respectively, and showed stability for 50 hours in a 1 M KOH and seawater electrolyte. Yu et

⁶ Uniformly isolated metal atoms exposed on a conductive substrate to maximize atom utilisation efficiency and heighten active site exposure [35].

al. [49] developed the three-dimensional NF structure further by designing NiFeN nanoparticles on NiMoN nanorods. Tested in similar conditions of 1M KOH and seawater, this catalyst showed better results than the aforementioned ones, reaching potentials of 1.6, 1.8 and 1.9 V at current densities of 100, 500 and 1000 mA/cm², respectively.

Luo et al. [38] focused on a different morphology, investigating a spherical structure with nanocubes $Ni_3S_2@NiFePBA/NF$. Tested in seawater (from Liaoning, China) mixed with 1M KOH as a buffer to reach alkaline conditions, it reached an overpotential of 351 mV at a current density of 1 000 mA/cm². This catalyst showed stability for 225 hours and a faradaic efficiency of 96%.

Iron and phosphor dual-doped nickel selenide (Fe,P-NiSe₂) nanoporous films have been proposed as bifunctional catalysts by Chang et al. [41]. The iron-dopant was identified as the primary active site for the HER. In the experimental validation, a current density of 0.8 A/cm² was achieved at a potential of 1.8 V with high OER selectivity and long-term stability for over 200 hours. Electrolysis efficiency for H₂ was reported to be above 78.4% at 1.6 V [41]. The HER/OER performance in natural seawater was worse than that shown in KOH-buffered electrolytes, but this was attributed to the low conductivity of the seawater.

4.2.3 Oxygen evolution reaction catalysts - cobalt-based

Cobalt-based catalysts have been studied because of their high activity even at a neutral pH (7-9); they are functional in salt-water and resistant to corrosion [43]. Song et al. [39] developed a carboncoated sodium cobalt-iron pyrophosphate ($Na_2Co_{1-x}Fe_xP_2O_7/C$) nanoparticle (NCFPO/C NP) electrode, the efficiency of which is controlled by the Co/Fe ratio. The catalyst was tested in seawater from Incheon, South Korea, after adding KOH to increase the pH to 13 and precipitate Mg(OH)₂ and Ca(OH)₂. The water was further filtrated by centrifugation. The catalyst was effective in avoiding the production of chlorine species. The measured overpotential was less than 480 mV for a current density of 100 mA/cm². Durability tests were performed for 100 hours.

Zhao et al. [51], on the other hand, developed a three-dimensional free standing cobalt selenide (CoSe) electrode that can work both as an anode and a cathode. It was tested in seawater from Adelaide, Australia with the addition of KOH and a buffer solution to reach a pH of 7 without further purification. The results showed a potential of 1.8 V for a current density of 10 mA/cm².

In addition to a bifunctional cobalt-based catalyst (CoO_x on carbon fibres), Guo et al. [36] tested the use of a hard Lewis acid (Cr₂O₃) in order to achieve seawater splitting at neutral conditions and to avoid the use of KOH solutions. When a layer of Cr₂O₃ is applied to the catalyst, the water near the surface has a faster dissociation kinetic, forming a high concentration of OH⁻. At the same time the H⁺ formed by the water dissociation is driven away by the electric field, thus increasing the local alkalinity. This local alkalinity reduces the presence of Cl⁻ ions due to the higher concentration of OH⁻, and reduces the presence of precipitates due to the OH⁻ binding more strongly with Lewis acid than with the cations present in seawater. The test was conducted with a flow-type electrolyser, using water from the Huanghai Sea, China that was filtered to remove solids and microorganisms. The test showed a current density of 1 A/cm² at a potential of 2.3 V, which lowered to 1.9 V when the operating temperature was raised from 25 °C to 60 °C. The durability test was run for 100 hours; but the faradaic efficiency was 93% for hydrogen and 92% for O₂.

Iron oxyhydroxide (FeOOH) on a cobalt base has been explored as OER catalyst material. Oxyhydroxide species are considered to be the active sites for OER. A heterogeneous cobalt phosphide (CoP_x, CoP-CoP₂) was used as the core to construct core-shell-structured CoP_x@FeOOH [55]. The authors reported that this catalyst exhibited advantageous properties, enabling high current densities. In combination with the HER-active CoP_x core, the CoP_x and $CoP_x@FeOOH$ electrodes required voltages of 1.7 and 1.9 V to attain current densities of 100 and 500 mA/cm², respectively, in a 1 M KOH seawater electrolyte [55].

4.2.4 Oxygen evolution reaction catalysts – cobalt and nickel based

As mentioned in Section 4.2.2, NF acts as a conductive substrate with a three-dimensional structure that facilitates bubble release and electrolyte diffusion on the active surface. Wu et al. [40] developed a boron-modified cobalt-iron (B-Co₂Fe) LDH on an NF substrate. The boron modification was used to increase the electric conductivity of the catalyst. In 1 M KOH seawater (from Galveston, Texas, United States, without further purification), the catalyst showed overpotentials of 245, 310, 376 and 415 mV for current densities of 10, 100, 500 and 1000 mA/cm², respectively, with a faradaic efficiency for the OER of 98%. The catalyst showed a slight efficiency decrease after testing for more than 100 hours due to the obstruction of the active sites by chlorine ions and insoluble precipitates. Hypochlorite products were not detected, however. Another anodic catalyst consisting of three-dimensional standing arrays of Ni/Co nanosheets on NF enabled high current densities, which were tested up to 800 mA/cm², necessitating a voltage of 2.1 V. The process remained reasonably stable for about 100 hours, with a fluctuation in voltage of less than 10 % [56].

Similarly, Wang et al. [45] used a Co-Fe₂P catalyst grown on NF as a bifunctional electrode. The tests, conducted in simulated seawater (the content of which was not specified) showed a working potential of 1.7 V at 100 mA/cm² with stability for 22 hours and no detection of hypochlorite products. Wu et al. [46] developed a non-ferrous bifunctional electrocatalyst, Ru-CoO_x/NF, showing overpotentials of 630 and 1390 mV at 100 and 1000 mA/cm², respectively, in alkaline seawater.

4.2.5 Oxygen evolution reaction catalysts - other

Hsu et al. [57] designed a transition metal hexacyanometallate (MHCM) based catalyst with the help of density functional theory calculations. A thin shell of MHCM was layered over basic cobalt carbonate (BCC) in a core–shell nanoarchitecture. The electrode demonstrated good selectivity towards the OER in buffered neutral seawater. A voltage of 2.1 V was required to generate a current density of 10 mA/cm² for the tested MHCM-z-BCC/NiMoS combination [57].

4.3 Asymmetric electrolyte feed

In most designs of seawater electrolysers, both the anode and the cathode use the same alkalinised seawater electrolyte. However, the need for limiting the anode potential to $1.7 V_{rhe}^{2}$ to guarantee 100% oxygen selectivity leads to low electrolyser cell current densities. Therefore, several researchers have investigated approaches using separate anode and cathode compartments, typically with seawater being supplied to the cathode and an alkaline electrolyte being supplied to

⁷ RHE denotes Reversible Hydrogen Electrode

the anode. This configuration could potentially increase the performance of seawater electrolysers and lower the requirement for KOH [58].

In a study by Dresp et al. [58], a configuration was investigated that involved feeding neutral seawater directly to the cathode while circulating a pure KOH electrolyte at the anode. The researchers used a NiFe-LDH catalyst. This is a further development of the catalyst material as described in Section 4.2.2 [3], which in this study exhibited good catalytic activity and OER selectivity compared with conventional iridium-based benchmark catalysts [58]. The NiFe-LDH catalyst maintained selectivity the OER even at high cell voltages of up to 4.0 V_{cell}, and suppressed the CER. The researchers found that the NiFe-LDH catalyst did not oxidize the Cl⁻, although trace amounts of Cl⁻ ions crossed the membrane and reached the anode compartment. The authors proposed that investigating the exact catalytic mechanism behind this CER suppression is necessary.

Frisch et al. [59] proposed an asymmetric-feed electrolyser design, utilizing PGM-free materials. The design includes cobalt- and nickel-based phosphides/chalcogenides, which serve as electrocatalysts, as well as porous transport layer surface coatings. The catalysts and porous transport layers were integrated into an MEA employing a customised terphenyl-based AEM. The electrolyser operated at current densities of up to 1.0 A/cm² at a voltage below 2.0 V under synthetic alkaline seawater and dry cathode conditions.

4.4 Alternative oxidation reactions

Alternative reactions to chlorine formation have been suggested, wherein specific chemicals (e.g. hydrazine or urea) can act as sacrificial agents, allowing the anodic reaction to proceed at more favourable energy levels than both the OER and the CER [60]. These concepts also follow an asymmetric feed approach.

The replacement of the OER with faster electro-oxidation reactions of lower potential, such as a sulphion (S²⁻) oxidation reaction, has been explored [61]. The sulphion oxidation reaction has a lower oxidation potential of – 0.48 V and faster kinetics involving fewer electrons. This helps to avoid chlorine chemistry in seawater electrolysis and reduces energy demand, so that water splitting can occur below 1.0 V [61]. According to the authors, this would enable a reduction of the energy demand by 50%. An additional benefit lies in the possible degradation of toxic H₂S or S²⁻ pollutants in industrial exhaust gas and sewage into valuable sulphur. An asymmetric electrolyser is proposed by the authors, with seawater in the cathode chamber and sulfion on the anode side. The electrodes were based on CoO (for the cathode) and CoS₂ (for the anode). A hydrogen generation rate of 5.3 mol/h g/catalyst was achieved, and the faradaic efficiency of 96% was maintained for 180 hours at 300 mA/cm² [61].

A hybrid approach, combining an asymmetric feed and an alternative reaction based on hydrazine decomposition was proposed by Sun et al. [60]. Seawater was used as the catholyte and 1M KOH with 0.5M hydrazine as the anolyte feed. NiCo based identical electrodes were separated by an AEM. The OH⁻ ion was transported to the anode side where a hydrazine degradation reaction occurred, to nitrogen and water. This concept enables the use of low cell voltages between 0.7 and 1.0 V but current densities of 500 mA/cm², leading to an electricity demand as low as 31 kWh/kg H₂ [60]. Further improvement of the AEM is needed in order to advance this concept, according to the authors.

4.5 Membranes for seawater electrolysis

As evident in the previous sections, significant efforts have been made regarding the improvement of catalysts, in particular for the OER. Membranes and ionomers have not been studied to the same degree, even though there are performance issues and gaps in knowledge [62]. For this review, we could not identify many papers focusing on membrane⁸ development specifically for DSE (except [59], see below).

4.5.1 Conventional⁹ membranes or diaphragms

4.5.1.1 Anion exchange membrane

AEM electrolysis (AEMEL) is considered a technology well suited for seawater splitting [63]. Water is fed to either the cathode, the anode, or both. As AEMEL operates in an alkaline environment, the OER kinetics are favoured for lower overpotentials, and non-precious-metal (e.g., Ni-,Fe-,or Co-based) catalysts can be used.

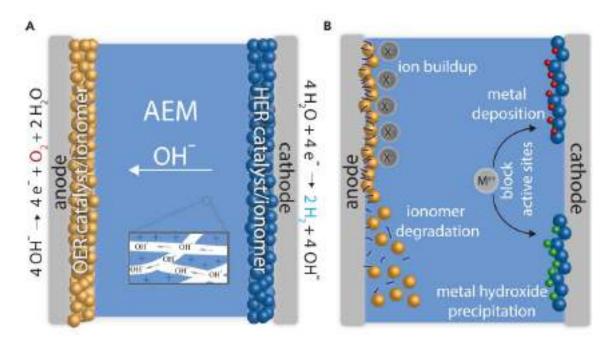
The European Innovation Council-funded ANEMEL project [4] conducts research on electrolysis to improve its efficient functioning with impure water, such as saline and waste water sources. In one of its work packages, the project is developing fluorine-free composite membranes, after finding that adding cerium oxide helped improve the stability of the polymer membrane [64].

Lindquist et al. [62] summarised the state of the art and the development needs for AEMEL for seawater electrolysis. **Figure 7**B provides an overview of the possible degradation mechanisms. Water-transport limitations enhance degradation by increasing local OH- concentration, breaking down the membrane structure. Fenton oxidation processes, involving Fe species, can also degrade the ionomer and the membrane. As many of the non-PGM catalysts being investigated contain Fe, this needs further investigation. In the case of asymmetric feeding (see also Section 4.3), the membrane must be developed further to prevent cathode dehydration. Many of these degradation pathways could be addressed by polymer development. Lindquist et al. [62] also mention that maintaining a high level of hydration in the membrane can help mitigate chemical degradation.

⁹ Used for water electrolysis.

⁸ Two types of membranes are typically utilised in electrolytic cells: porous media membranes and ion-exchange membranes. Diaphragms are a type of porous media membrane and are made of a typically self-supporting microporous material with a pore size of less than 1 µm to enable ion selectivity. Porous membranes act as a barrier, restricting the transport of molecular and ionic species between the electrolyte compartments by hindering convective flow and molecular diffusion. On the other hand, ion exchange membranes facilitate the movement of either anions or cations, while efficiently blocking counter-ions and potentially neutral molecules [127]. In general, films that have charged groups are known as ion-exchange membranes. These membranes are composed of polymer or ceramic matrices with either positive or negative charges fixed in them. The characteristics and manufacturing methods of ion-exchange membranes are closely tied to those of ion-exchange resins, which are commonly used for water purification.

Figure 7 Schematic of AEMEL and possible degradation modes. (A) Asymmetric AEMEL: The concept of asymmetric feeding of the electrolyte is also further explored in section 4.3. (B) Possible electrolyser degradation mechanisms due to impurities [62].



Source: Lindquist et al. [62] © 2020, Elsevier Inc. All rights reserved.

Dresp et al. [3] proposed that the abrupt drop in current density they found when performing experiments in seawater is due to a decline in the ionic OH– membrane conductivity. The presence of chloride ions reduced the OH⁻ transference numbers across the AEM channels, poisoning the cationic side groups of the ionomer. Consequently, this leads to a decrease in the effective transport of OH⁻ ions across the membrane to the catalyst layers, resulting in a diminished current density. The authors stated that the migration of OH⁻ ions through the anion-conducting membrane seems to be the rate-limiting step and dictates the overall catalytic current density.

Frisch et al. [59] developed a custom biphenyl-based ionomer with good properties compared with commercial AEMs (see also Section 4.3). This is the only example we could find of membrane development, and the authors also emphasised the importance of further research, in particular for asymmetric feed-type devices [59].

4.5.1.2 Proton exchange membrane

In several studies, Nafion membranes were used (e.g. in Hu et al. [65]), or a Nafion solution was part of the catalyst preparation (e.g. in [57]). As PEMELs operate in acidic conditions, which favour chlorine evolution over that of oxygen, few researchers have worked with this type of electrolyser for seawater electrolysis. A PEMEL flow type setup was used by Guo et al. [36], achieving a current density of 1 A/cm², (see Section 4.2.3). Rossi et al. [66] found that the negative charges of the sulphonated groups within the PEM impeded the movement of Cl⁻ towards the anode and they attributed this to electrostatic repulsion. Different thicknesses of Nafion were investigated; the thicker membrane reduced sodium contamination, but the maximum current density had to be lowered significantly. A Nafion membrane was also used to protect the electrode in an older study [67], but few studies are targeting the use of this type of membrane for DSE, and we did not find any mention of further developments.

4.5.1.3 Alkaline water electrolysis-type diaphragms

In contrast to membranes used in PEMEL or AEMEL, the diaphragm materials (e.g. Zirfon) used in AWE exhibit greater physical durability and are less susceptible to pore blockage. However, as anions or cations (e.g. H⁺, Na⁺, OH⁻, and Cl⁻) can migrate across the diaphragm, the use of these types of materials poses significant challenges in the design of seawater-splitting systems [52]. Based on the papers considered, it seems that little research has been conducted on AWE-type concepts for this purpose.

4.5.2 Non-conventional membranes

Membrane types that are not typically used for water electrolysis have been explored for DSE. In some cases they are employed instead of an AEM or PEM, and in other cases they serve to purify the seawater before water splitting. Such non-conventional membranes could be other types of ion exchange membranes including bipolar membranes, composite membranes or non-ion conducting perfluoropolymers-type membranes.

4.5.2.1 Bipolar membranes

Bipolar membranes (BPMs) are used for water purification through electrodialysis (see also Section 5.2), and can be classified as a type of ion-exchange membrane. They consist of a cation-exchange layer and an anion-exchange layer, which enables the formation of protons and hydroxide ions via a water dissociation mechanism [68]. In between these two layers is what is called the bipolar junction. Unlike conventional ion exchange membranes, BPMs are not supposed to allow ion transport across them. The main function of a BPM is the water dissociation at the bipolar junction.

BPMs have been used as separators in asymmetric setups (see also Section 4.3) for DSE. This supports the retention of dissimilar catholytes and anolytes as well as keeping the electrolyte concentration and the pH stable during electrolysis. The water dissociation in the BPM replenishes the electrolyte with protons and hydroxide ions, maintaining the electrolyte level and concentration. This reduces the need for electrolyte supplementation. A study by Han et al. [69] reported that through using a BPM the catholyte (natural seawater) was acidified to a pH of 2 by the protons from the water dissociation [69]. This prevented the formation of inorganic deposits on the cathode and reduced the cell voltage. The supply of hydroxide ions from the BPM enabled the retention of the anolyte alkaline at approximately a pH of 13, which is sufficiently high for the selective OER in the presence of Cl⁻ ions. The use of a BPM can have benefits for DSE; however, the extra energy demand of the water dissociation, which requires a thermodynamic potential of ~0.8 V, has to be considered.

Marin et al. [70] compared the performance of a PEMEL and a BPM electrolyser for DSE, finding that in asymmetric seawater conditions, the PEMEL ceased functioning after 50 hours and produced a higher amount of free chlorine (20 μ M) within the initial 24 hours than the BPM electrolyser did during its operation over 100 hours. However, both systems saw decreased voltage stability when fed with seawater, and the authors concluded that there were other failure mechanisms beside the effects of chlorine, probably stemming from the more complex electrolyte composition.

4.5.2.2 Composite membranes

As an alternative to ion exchange membranes for DSE, thin film composite (TFC) membranes, also referred to as semipermeable membranes, have been suggested by several researchers, such as Shi et al. [71]. TFC membranes are typically employed for water purification, for example in reverse

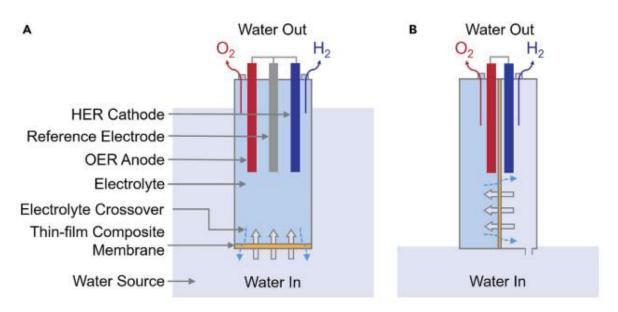
osmosis (RO) or forward osmosis (FO) ¹⁰ plants (see also Section 5.2 for an overview). This type of membrane can be considered a kind of molecular sieve, consisting of one or more active layers, such as a selective polyamide, which are deposited on a porous layer and a support layer.

For ion exchange membranes there is a trade-off between ion conductivity and selectivity, as selectivity typically decreases with an increase in ion conductivity [72]. In order to have highly conductive ion-exchange membranes, a high ion-exchange capacity is required, which, however, leads to low ion selectivity. Porous membranes can be considered an alternative, as the selective layer and porous support can be independently designed with the desired properties. Depending on the pore size of the selective film, RO/FO membranes can be fabricated to be highly selective for small ions, allowing the transport of protons and OH⁻ ions while restricting the passage of larger ions such as Na⁺ and Cl⁻[71]. These types of membranes have other advantages, such as much lower costs than ion exchange membranes. A disadvantage is the higher electrical resistance than that of Nafion membranes [71]. RO membranes need to be more robust, as the RO process utilises a pressure differential (see Section 5.2).

For DSE, TFC membranes can be used in two different manners, either to block ions, effectively purifying seawater before it reaches the anode or the cathode, or as a separator between the electrodes, enabling asymmetric electrolytes (see **Figure 8**, which shows two variants, one based on FO, the other on RO). The membrane can also be used to build up pressure between the electrolyte chambers, concentrating the evolved hydrogen gas [71].

¹⁰ FO is a process that involves a semipermeable membrane used to separate water from dissolved solutes by; employing an osmotic pressure gradient. The membrane permits the passage of water molecules while retaining dissolved solutes on the other side. In contrast, RO employs hydraulic pressure as the force driving separation. This pressure opposes the osmotic pressure gradient, thereby preventing water flow from the permeate to the feed. For FO, efforts are ongoing to develop suitable membranes as there are issues with mechanical stability, internal concentration polarisation and fouling. For an overview, see [128].

Figure 8 Electrochemical seawater splitting based on reverse or forward osmosis, schematic from [73]. A: a forward-osmosis water-splitting cell and B: the membrane is placed between the two electrodes forming two separate chambers with the desalinated water drawn from the catholyte.



Source: Logan et al. [73] © 2021, Elsevier Inc. All rights reserved.

A membraneless (apart from the water purification membrane) setup shown in **Figure 8**A has been investigated by Veroneau et al. [74]. A membrane is placed at the bottom of the cell, where desalinated water crosses into the electrolyte due to its higher osmotic pressure. In an FO water-splitting cell operating for four days, the cathode surface only showed a minimal accumulation of Mg^{2+} or Ca^{2+} (less than 0.5% by weight). Despite this, the catalytic activity remained constant throughout this period. This was attributed to the selective semipermeable membrane and the buffered internal compartment (0.6M NaH₂PO₄/Na₂HPO₄) in the cell, which worked together to control the pH gradient at the cathode [74]. The authors note that long term operation would lead to deterioration of the membrane and that new semipermeable membranes would be needed.

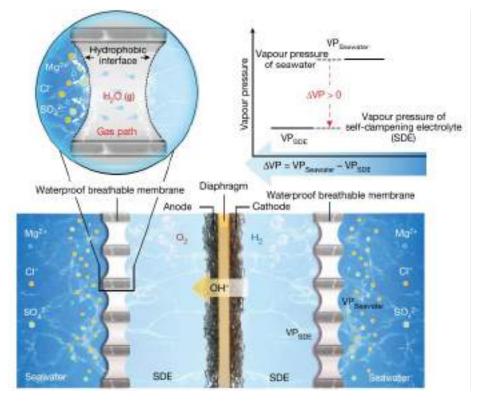
For a TFC membrane used as a separator between the electrodes (see **Figure 8**B), studies by Shi et al. [71], [75] showed that the active layer of the composite membrane was able to reject the transport of larger hydrated salt ions but allowed smaller protons and hydroxide ions to pass through as balancing charges. Therefore, the ability of these TFC membranes to efficiently transport protons or hydroxide ions and reject the larger salt ions makes them a promising option for use in DSE, especially in the presence of impurities in the electrolytes. The RO membrane resistance was 21.7 \pm 3.5 Ω cm² in 1M NaCl and the voltages needed to split water in a model electrolysis cell at current densities of 10–40 mA/cm² were comparable to those found for ion exchange membranes [71]. According to Logan et al. [73], this design is also likely to have salt ion crossover challenges, due to chloride ion transport through the RO membrane. However, Shi et al. [71] found a significantly lower chloride ion crossover with the TFC membrane, than with a cation exchange membrane (CEM). In general, both RO- and FO- based systems need to further improve membrane performance with regard to durability and the minimisation of the crossover of unwanted ions.

4.5.2.3 Polytetrafluoroethylene membranes

Polytetrafluoroethylene (PTFE) membranes, have garnered considerable interest from researchers due to their unique properties. PTFE is strong, chemically resistant, and extremely hydrophobic

because of fluorine's high electronegativity. Consequently, PTFE is widely used in diverse applications such as liquid/air separation.

Figure 9 Schematic depicting the liquid–gas–liquid phase transition-based migration mechanism of the water purification and migration process and its driving force [76]. SDE, self-dampening electrolyte



Source: Xie et al. [76] © 2021, The Author(s), under exclusive licence to Springer Nature Limited. All rights reserved.

PTFE membranes have been used for the purification of seawater in an integrated device, as proposed by Xie et al. [76] (see **Figure 9**). Water is purified by means of a hydrophobic porous PTFE-based membrane that blocks liquid water, letting through water vapour. The electrolyser consists of a self-dampening electrolyte (SDE)¹¹, which is composed of a concentrated KOH buffer solution, a hydrophilic diaphragm and electrodes. The anode uses a Mo-Ni-based catalyst and the cathode a commercial PtNi mesh. The driving force for water migration from seawater to the SDE is the difference in water vapour pressure. The mass transfer across the PTFE membrane takes place through a liquid-gas-liquid phase transition. This involves the evaporation of liquid water into a gaseous state on the seawater side, followed by migration across the membrane as gaseous water. The gaseous water then liquefies again by absorption within the SDE. According to the authors, this water purification mechanism enables ion blocking and has a high water-migration rate and antifouling capabilities. A prototype was demonstrated at 250 mA/cm² for over 3 200 hours, generating 386 litres of hydrogen per hour with an energy consumption of 55.6 kWh/kg H₂. It exhibited no significant corrosion or membrane wetting issues. However, the authors state that for longer operation periods, the risk of membrane wetting and fouling has to be considered [76].

¹¹ An SDE generally has four stages of the self-dampening process: dry crystals, a mixture of crystals and saturated solution, a saturated solution, and a dilute solution [76].

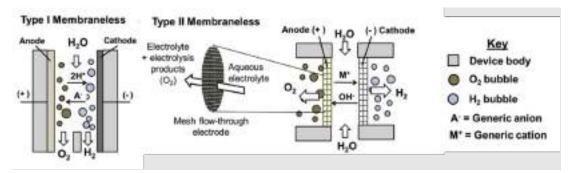
In terms of the methods shown in **Figure 8**, this work can be considered a combination of method in panel A and a conventional alkaline electrolyser.

This approach was demonstrated in collaboration with the Dongfang Electric Corporation in China, in the floating offshore wind power direct electrolysis hydrogen production platform called Dongfu No. 1. The trial was conducted from 17 to 26 May 2023, in Xinghua Bay, Fuqing City, Fujian Province, China. During this trial, the hydrogen production scale reached 1.2 Nm³ H₂/h, with an electrolysis energy demand of 55.6 kWh/kg H₂. The platform was operating for more than 240 hours in an actual marine environment, maintaining an ion barrier rate of over 99.99% for seawater impurities and producing hydrogen with a purity level of >99.9% [77], [78]. No fouling of the PTFE membrane was detected after the 10 days of operation. The researchers found that the maritime environment was not detrimental to hydrogen production, although a dehumidification system and an air circulation system needed to be added to prevent corrosion. However, to ensure the suitability of a floating platform for deep-sea use, they stated that it is necessary to address the platform's resistance to stronger winds and waves. Additionally, the stability and durability of the hydrophobic porous membrane and the electrolysis system must be enhanced for sustained performance in controlled oceanic conditions over time [77].

4.6 Membraneless electrolysis

In conventional electrolysers, either a membrane or a diaphragm transport ions between the electrodes and simultaneously separate the H₂ and O₂ gases that could otherwise form an explosive mixture. Membrane-less electrolysers are based on the flow- or buoyancy-induced separation of the gaseous oxygen and hydrogen products before they cross over to the opposing electrode. In general, two different options have been investigated. These two types are distinguished by the arrangement and configuration of their electrodes. In Type I electrolysers, the electrolyte flows parallel to the electrode surfaces. Type II electrolysers use a flow-through electrode design, where the electrolyte passes through porous electrodes, which allows the hydrogen and oxygen gas products to be carried into separate channels (see **Figure 10**) [79]. Not using a membrane could reduce costs and avoid issues like membrane fouling, with the trade-off being that gas separation is more challenging.

Figure 10 Schematics of membraneless electrolysers based on (left) flow-by electrodes and (right) flow-through electrodes. The inset in (right) shows a view of a mesh flow-through electrode evolving O_2 as electrolyte passes through holes in the mesh, adapted from [79].



Source: Esposito [79] © 2017 Elsevier Inc. All rights reserved.

The flow-through approach was chosen by Davies et al. [80], utilising catalyst-coated mesh flowthrough electrodes. Product cross-over rates were reduced to 1% when the active platinum catalyst was deposited only onto the electrodes' outer surfaces. This enabled the evolution of gaseous hydrogen and oxygen products only on the outer surfaces of the electrodes; this evolution was followed by buoyancy-driven separation of the gases into separate overhead collection chambers. The experiments were not performed with seawater, but in 0.5 M H_2SO_4 as the electrolyte.

A flow-by electrolyser was demonstrated, using a CER-selective anode and HER-selective cathode pair. The system produced hydrogen and HClO from unbuffered seawater used as electrolyte [81]. This process involved developing chlorine-oxidation-selective anodes and chlorine-reduction-inhibitive cathodes, with the aim of hindering the OER at the anode and maximising the HER at the cathode. With the coupling of these two reactions, high-purity H₂ gas could be produced without the presence of O₂, eliminating the need for a membrane as the generated chlorine remained in the aqueous phase. MnOx as the cathode material for the HER enabled the complete inhibition of chlorine reduction. An optimised ternary PRT (Pt, Ru and Ti) electrocatalyst maintained good stability with constant HClO activity over 500 hours under severe conditions. The study demonstrated the successful operation of the PRT anode/MnO_x cathode pair in producing hydrogen gas at an efficiency of ~100% via seawater electrolysis at a pH of 8.2 over 100 hours in a membraneless reactor. No oxygen evolved during the process, while HClO production occurred at an efficiency of ~100% [81].

Badreldin et al. [82] investigated symmetric and asymmetric recirculation schemes to facilitate pH rebalancing during electrolysis in buffered and unbuffered synthetic seawater electrolytes at nearneutral pH. They found minimal pH drift in the asymmetric system compared with a symmetric system, as changes in the pH of anolyte and catholyte effluent streams offset each other when fed to the opposing inlet stream. In the opinion of the authors, this makes the asymmetrically fed electrolyser suitable for unbuffered synthetic seawater electrolysis. A current density of 100 mA/cm² was achieved under asymmetrically fed flow-by parallel electrodes in 0.5M phosphate buffered synthetic seawater with a cell voltage of 2.61 V.

4.7 Solid oxide seawater electrolysis

Liu et al [83] employed solid oxide electrolysis (SOEL) to split untreated natural seawater, and analysed its electrochemical performance and long-term stability. The electrolysis process was conducted at a constant current density of 200 mA/cm² for 420 hours, producing 183 mL/min of hydrogen and showing a degradation rate of 4.0% over the operational time. An energy conversion efficiency of 73% was achieved without reusing the high-temperature exhaust gas. After 420 hours of experimentation, it was discovered that the structure and composition of the cell material remained stable, indicating that long-term operation had no significant effect on the cell itself. As for SOEL seawater is heated and evaporated, and the water vapour is largely free of salt and impurities. This helps to avoid many of the issues faced in DSE at low temperatures.

Luo et al. [84] studied the effects of seawater steam/H₂ hydrogen ratio, temperature and current density on the conductivity and structure of flat-tube SOE cells. The researchers found that a higher seawater content in the gas mixture (hydrogen was used as a carrier gas) positively impacted the conductivity of the Ni-3YSZ support, while the conductivity decreased with rising operating temperature. Durability tests at the cell level of over 500 hours were conducted, and the degradation rate of area-specific resistance was determined to be 0.207 m $\Omega \cdot cm^2/100$ h at a current density of 1 000 mA/cm². According to the authors, seawater steam caused agglomeration and loss of Ni particles in the fuel electrode support after the long-term test, with more distinct effects observed under high current density.

4.8 Other water splitting concepts

An integrated device for hydrogen generation, using osmosis to generate electricity has been demonstrated to operate for up to 12 days and reach a hydrogen production rate of ~316 l/m²/h [85]. Osmotic power generation technology converts the osmotic energy found at the interface of seawater and freshwater into electrical energy (estimated at 0.8 kWh/m³), which is then transformed into hydrogen through electrolysis [85]. The laboratory-scale device enables ion transport and electron transfer within a single circuit. The bioinspired membrane selectively transports Na⁺ ions across the seawater-freshwater interface, converting ion transport signals into electricity. On the electrode surface, an electric field is generated within the alkaline electrolyte. This electric field drives the generation of oxygen at the anode surface and hydrogen at the cathode surface. According to the authors, the device can produce hydrogen at a much higher rate and with less electricity consumption (reduction of ~40 kWh/kgH₂) than commercial water-splitting devices [85].

A similar concept is reverse electrodialysis (RED) to harness salinity gradient energy. A RED stack is comprised of alternating AEMs and cation-exchange membranes (CEM) and a redox electrode pair. When high-concentration and low-concentration solutions flow through the compartments, the anions and cations on the high concentration side move to the low concentration side via the AEMs and CEMs, respectively. This movement generates a voltage difference across each membrane. This process thereby converts the salinity gradient, which would otherwise dissipate during uncontrolled mixing, into an ionic current and subsequently into electricity at the electrodes. Stacking multiple CEM and AEM pairs enables a larger total voltage to be obtained. The salinity gradient can be used to either generate electricity or to produce hydrogen directly. RED is the opposite of electrodialysis, a process commonly used for desalination [86]. A mathematical model for this RED-based system that converts low-grade thermal energies to hydrogen, driven by the membrane voltage sourced from the salinity gradient of potassium acetate solutions, has been reported [87]. In general, much of the research has been performed on ammonia bicarbonate or other salt solutions.

Experiments were carried out by Pellegrino et al. [88] with a RED electrolyser using water with different levels of NaCl salinity; they also compared this with assisted RED, in which additional electricity is used to drive the process. Various concentrated solutions were used, including one mimicking seawater at 35 g/l NaCl. Continuous tests were conducted under specific current conditions, which resulted in high faradaic efficiency. The study found that the assisted RED technology achieved the highest currents and productivity, with a maximum of 1.7 mol/h/m², with a high salinity solution of 300 g/l NaCl. An economic analysis was carried out, indicating that a minimum levelised cost of hydrogen (LCOH) of EUR 3.2/kg H₂ might be achievable at high salinity gradients, again with the 300 g/l NaCl solution [29]. This could be an option for how to utilise the brine produced by desalination plants. A disadvantage is that this technology operates at low current densities and hydrogen production rates.

An integrated method for generating hydrogen from seawater has been proposed [89], combining a microbial electrolysis cell (MEC) and a RED system. This concept is still at a low TRL, but could potentially lower the energy demand for electrolysis and in addition purify wastewater. The MEC oxidises organic matter through exoelectrogens on the anode, the resulting potential (up to 0.8 V), however, is not high enough to drive a water-splitting reaction. The RED system utilises the salinity gradient between seawater and river water, thereby meeting the additional energy demand. The advantage of integrating these systems is that the energy provided by the exoelectrogens in the MEC reduces the number of RED units needed, and that the current generated from the salinity gradient in the RED system eliminates the need for an external power source for the MEC.

5 Indirect seawater electrolysis

Although there is no harmonised terminology, ISE usually refers to the electrolysis of seawater that has been desalinated and purified by dedicated installations using conventional and mature desalination technologies. The seawater will then reach a similar purity level to the water directly fed to conventional electrolysis systems¹². Electrolysers typically have water purification systems included in the balance of plant, see also section 5.3 on water purity requirements.

This section provides an overview of the status and deployment, and the techno-economic description of commercially available desalination technologies. It also includes information about the impacts (mainly cost, land footprint and energy demand) generated to desalinating and purifying water, which come in addition to those generated by running the electrolyser.

5.1 Status and deployment of desalination plants

In 2022, there were more than 20 000 desalination plants operating worldwide with a total operating capacity of about 90 million m³/d [90]. Since 2000, the global number of desalination plants and their daily production capacity has doubled [91]. The desalinated water is used for either the industrial or the municipal sectors, the latter being the largest user, as 62.3 % of desalinated water is produced for human consumption [91]. In the EU, there are over 1 000 plants [92], mostly in the Mediterranean region, representing 10 % of the global desalination capacity [93]. The largest plant in Europe, with a capacity of 240 000 m³/d is located in Torrevieja, Spain and produces drinking-quality water [92].

The basic approaches to desalination can be categorised by their evaporation/condensation, filtration and crystallisation technologies (see Figure 11). Globally, the most commonly deployed of these are filtration/membrane-based approaches, such as RO (see **Figure 12**), as they offer lower operational costs. Thermal-based desalination plants are more often found in the Middle East, where low-cost fuels are available.

¹² Based on available information, the type of water used in currently operating electrolysers is assumed to be drinking water from water mains.

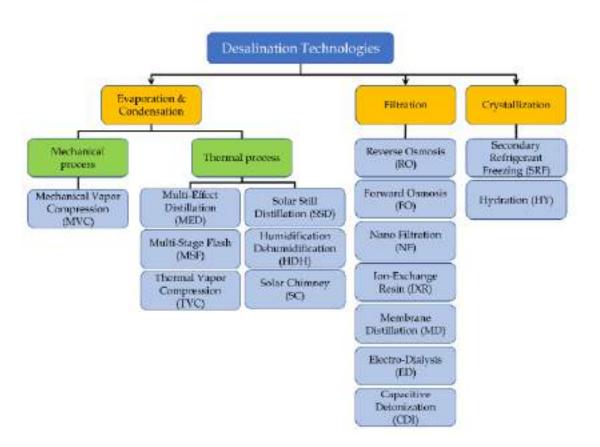


Figure 11 Classification of desalination technologies by working principle [94].

Source: Curto et al. [94] © 2021 by the authors. All rights reserved.

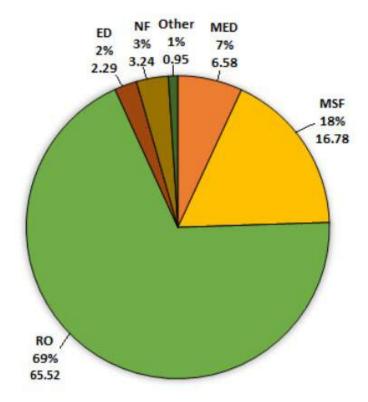


Figure 12 Global desalination capacity per type of technology in 2020 [95]. ED, electrodialysis; MED, multieffect desalination; MSF, multistage flash desalination

Source: Greco et al. [95] © 2021 published by MDPI under CC BY license.

Table 3 Overview of desalination technologies using data from various sources. MD, membrane distillation;MED, multi-effect desalination; MSF, multistage flash desalination.

Properties	MSF	MED	RO	Electrodialysis	MD
Typical plant size (1000m ³ /day)	50-70	5-15	Up to 624	2-145	0.05 - 0.1
Recovery ratio (^a) (%)	30-45	30-45	35-50	50-90	Up to 98
Tolerated feed salinity (ppm)	No restrictions	No restrictions	30 000 – 60 000	<5000	No re- strictions
Thermal energy (MJ/m ³)	190–282	145–230	None	None	4–40 [96]
Electrical energy (kWh/m ³)	2.5–5	2–2.5	4-6	2.64-5.5	1.5-4 [96]
Total energy (kWh/m ³)	18.3-28.5	14.2-21.6	4-6	2.64-5.5	3-22 [96]
Product water quality (ppm im- purities(^b))	2-10	<10	<300-500 single pass	150-500	<10
Product water cost (USD, unless stated otherwise)	0.8-1.6	0.7-1.2	0.5-1.2	0.5-1.3	Estimated at EUR 5.40 – 9.60(^c) [97]
Source (entire column, unless stated otherwise)	[98]	[98]	[98]	[98]	[99]

(a) The recovery ratio in desalination signifies the proportion of feed water transformed into product water (fresh water) throughout the desalination process. It serves as a measure of efficiency regarding water recovery and is determined by dividing the volume of product water by the volume of feed water. A greater recovery ratio implies more effective water recovery in the desalination process.

(^b) Drinking water quality varies widely, but water with total dissolved solids values under 600 ppm can be considered potable according to the World Health Organization [129].

(^c) Powered by electricity. The use of solar or waste heat would lead to much lower costs [97].

5.2 Filtration-based desalination technologies

RO systems remove salt from seawater through osmosis, applying pressure to push water through a series of semi-permeable membranes. The external pressure has to be greater than the osmotic pressure to extract the solvent [94]. This technology has improved significantly over the years in terms of energy efficiency, for example through the development of more permeable membranes and by adding energy recovery devices for the pressure energy¹³ [100]. For seawater, which has a high amount of impurities, pre-treatment such as ultrafiltration, sediment filters, FO or activated carbon adsorption is needed. RO is the most common desalination technology globally, due to the high energy efficiency of the process for which the energy demand is in the range of 4 - 6 kWh/m³ (see **Table 3**).

¹³ Energy recovery devices can convert hydraulic energy into mechanical energy to drive a piston or pump, which transfers hydraulic energy back into the feed, for more information see [130].

An important parameter in terms of water use is the water recovery ratio (RR), which is the proportion of intake water converted into high quality water. Brine production is inversely correlated to the RR, with high RR leading to less, but more saline brine. Brine is commonly disposed of directly into saline surface water. This method raises environmental concerns, like risks to ocean life and marine ecosystems [91]. These risks can potentially be reduced or mitigated with proper brine release strategies [101]. The high RR of the RO process produces a very concentrated brine, containing almost all liquid waste, including chemicals used for pre-treatment.

The cost of 1 cubic meter of desalinated water produced using RO technology ranges from USD 0.5 to USD 1.2 $/m^3$, depending on the size and energy demand of the plant (see **Table 3**).

Electrodialysis uses a series of ionic membranes to separate ions. Electricity is used to provide a direct current between electrodes [98]. This technology is only suitable for brackish water without further pre-processing (see **Table 3**). Nanofiltration is another type of membrane technology that can be used to purify water with low saline content, based on membranes such as PTFE (see Section 4.5.2.3).

The resulting water purity of RO and electrodialysis is lower than that of evaporation based desalination techniques (see **Table 3**). The water produced by the Torrevieja RO desalination facility is used 50 % for irrigation and 50 % for domestic consumption, with <300 ppm total dissolved solids [102].

5.3 Evaporation/condensation-based desalination technologies

Evaporation/condensation-based desalination technologies use heat to evaporate water. Internationally, large scale evaporation-based desalination technologies have been deployed, most commonly multi-stage flash desalination (MSF) and multi-effect desalination (MED). The MSF process is a method of purifying seawater by means of the conversion of a part of the water into steam in several stages, which are essentially counter-current heat exchangers. MSF systems can consist of up to 30 stages. The process begins with heated saline water entering the first stage, which features lower ambient pressure than the brine heater pressure. As a result, this pressure differential triggers the flashing process of the saline water. The heat of condensation is transferred to the incoming saline feed water. Meanwhile, the distillate water is collected on a tray. Simultaneously, the remaining saline water advances to the subsequent stage, characterized by lower pressure. This process repeats in each stage until the saline water reaches the final stage, where it is then discharged [98]. For large-scale MSF plants, the total equivalent energy consumed is between 18.3 and 28.5 kWh/ m^3 [98] (see also **Table 3**). MED is more energy efficient, with a range from 14.2 to 21.6 kWh/m³ [98]. MED also involves several stages, often referred to as effects. In each stage, saline water is sprayed onto tubes, where it is heated by steam. A portion of the water evaporates, and the resulting steam travels through the tubes of the subsequent stage, serving to heat and evaporate more water. In the MED process, external steam is introduced solely in the initial stage. In subsequent stages, the energy removed by cooling is utilised as a heating source for the following stage. This is accomplished by systematically decreasing the pressure in each progressive stage [98]. Research is being conducted into improving the energy efficiency of thermal desalination processes, for example by using high vacuum pressure cascades [103]. The recovery ratio is improved in this process, with the improvement attributed to the high vacuum in the MED system. This enables a lowtemperature brine in the final stage and enables a higher salt concentration without the risk of crystallisation.

Thermal desalination produces a high volume of warm brine which needs to be disposed of. The quantity of brine release is up to five times higher but is less concentrated than that of filtration-based techniques [104].

Thermal processes offer a higher water purity than membrane desalination, but none of the technologies deliver purity levels suitable for direct use in a conventional PEMEL or AEMEL stack (see **Table 3**), necessitating further treatment. However, the water purity delivered to electrolysers operating today is likely to be drinking-quality water, and therefore also not sufficiently pure without further purification¹⁴. PEM and alkaline electrolysis need UPW to avoid performance degradation (see also Section 3).

5.4 Other desalination technologies and integration with external sources of heat

Other low-energy desalination technologies are under research and development and have not yet been scaled up for commercialisation. These include membrane distillation (MD), capacitive deionisation, pressure-retarded osmosis and adsorption desalination [98].

MD can be classified as either filtration or evaporation based, as it is a thermally driven process. Water is purified by vapour crossing a hydrophobic membrane due to a partial vapour pressure difference (see also Section 4.5.2). The necessary temperature gradient can be provided by low grade heat (gradient of 30–80 °C). In an MD process, the temperature difference at the membrane interfaces results in different vapour pressures of the constituents that are being separated, providing the driving force for separation. Liquid on the warm side, or the feed side, transforms into vapour at the feed membrane surface, traversing through the membrane pores to the membrane surface on the cold side, and thereafter condenses on the cold plate [105].

A laboratory-scale thermally integrated electrolyser and MD system has been successfully operated, showing that the purification system could run using the waste heat generated from the electrolyser [106]. The Sea2H2 project (2019-2022) [107] in the Netherlands has operated a 50 kW PEMEL thermally integrated with MD at a location close to the sea for approximately 1 000 hours [108]. The MD system produced more UPW than needed by the electrolyser. The public final report [108] does not provide information on the actual energy demand of the purification system. In 2023, Ohmium and Aquastill announced that they had entered into a partnership in order to advance the integration of PEM electrolysis with MD [109]. MD systems can recover up to 98 % of the water present in the feed [110].

Numerous modelling studies have been performed on the integration of MED and electrolysis, (for an overview see [111]); but the processes were not focussed on producing hydrogen.

The waste heat generated by the electrolyser can be used to improve the efficiency of desalination, for example, for RO, the flux through the membrane can be increased for a given pressure drop

¹⁴ For example with ion exchange resins, which can be used to achieve high-purity water by exchanging ions in the water with other ions immobilised on solid resin beads. There are four types of ion exchange resins: strong acid cations, weak acid cations, strong base anions, and weak base anions. Strong acid cations and strong base anions are commonly used for complete demineralisation, which is necessary for water electrolysis.

[112]. A study estimated that the energy efficiency of a PEMEL could be increased up to 15%, if the waste heat could be used by a heat consumer such as a desalination plant [113].

6 Energy demand, cost and land footprint estimates

There is not enough consistency and harmonisation of the performance measurements in the assessed papers to accurately compare DSE with ISE. Moreover, the TRLs of these technologies diverge considerably, with DSE mostly at around TRL 2. However, some rough estimates can be made for several important indicators, such as cost and energy demand.

6.1 Energy demand comparison

Energy demand varies widely for the different desalination processes, by more than an order of magnitude, ranging from 2.6 to 28.5 kWh/m³ (see **Table 3**). Filtration-based processes are generally more energy efficient than thermal desalination, as explained in Sections 5.2 and 5.3. Starting from Pacific Ocean water¹⁵ with total dissolved solids of 33.5 g/l, a typical seawater desalination plant would consume around 3.6 kWh/m³ [114]. If water consumption of 20 l/kg H₂ is assumed [115] (17.5 l/kg H₂ for PEM, 22.28 l/kg H₂ for AWE, excluding cooling water), this would correspond to an additional energy demand of 0.07 kWh/kg H₂ for electrolysis with desalinated water. Compared with the energy demand for electrolysis of around 50 kWh/kg H₂, the additional energy demand for desalination sunlikely to become a decisive factor.

Some papers stated that a significant reduction in energy demand and increased energy efficiency would be possible for DSE. These studies are not, however, based on standard water electrolysis concepts, but rather explore alternative oxidation reactions, with sulphion (S^{2-}) [61] or hydrazine [33]. In other studies, estimations of energy demand are in the range of 56 kWh/kg H₂ or higher (e.g. in [78]). In this respect the benefit of DSE in terms of energy efficiency is not evident.

6.2 Cost and business case advantages

The cost of water purified by desalination plants depends on a number of factors, such as the size of the plant, the type of desalination process and the salinity of the water to be treated. It ranges from 0.5 USD/m³ to 1.6 USD/m³ for large scale plants (see **Table 3**). For water from the Torrevieja plant, a cost of 1.20 EUR /m³ (2022) has been reported, compared with river water at 0.30 EUR /m³ [105]. The plant itself cost EUR 226 million [105]. A desalination plant in Barcelona with a similar capacity provides desalinated water at a cost of EUR 0.7/m³, whereas river water is priced at 0.2 EUR/m³ [106]. The additional cost of water from desalination could be estimated at roughly EUR 1/m³, this would add a total of 0.02 EUR/kg H₂. This is in line with similar calculations found in the literature [116], and, similarly to energy demand, is not a major cost item. However, there will be cost and energy savings for DSE if no further purification of UPW is needed. If, as a very rough estimate, the additional cost of UPW is EUR 1/m³, this would reduce the cost of hydrogen through DSE by around 0.02 EUR/kg H₂.

Other benefits could arise from the co-production of valuable materials such as bromine, magnesium or lithium, but it is not yet clear if DSE approaches would have an advantage over ISE in this respect.

¹⁵ The salinity and pH of seawater varies widely. The Baltic Sea exhibits the lowest salinity, and the Red Sea the highest. The average salinities for these two seas are approximately 7 ppt and 39 ppt, respectively. Among oceans, the Atlantic has the highest average salinity at around 36 ppt [131].

There are efforts ongoing to generate commercially valuable products from brine; for example, in Saudi Arabia an NF plant is extracting magnesium as part of a commercial-scale project [117]. Shahk et al. [117] investigated the feasibility of harvesting products from brine rather than from seawater, and concluded that focusing on processing vast amounts of seawater desalination brine to extract a single component other than NaCl would be less competitive than integrated processes aimed at obtaining multiple commercial species from the concentrate. In the opinion of the authors, regarding separation, a lengthy series of complex steps treating the entire volume of concentrate is unlikely to become viable, so the most promising separation technologies are those, such as NF, that separate the brine into streams enriched or depleted in entire classes of constituents with minimal energy and reagent input. It would be interesting to investigate whether DSE could have an advantage over RO desalination in this respect, although the low volumes of brine produced are likely to be unfavourable for commercially feasible recovery. A promising option offering economic benefit is the use of DSE for the co-production of hydrogen and other valuable products such as lithium, magnesium or chlorine, which warrants further investigation [20].

For DSE, most experiments are performed on a laboratory scale, with few durability tests lasting more than 1000 hours. Therefore, the maturity of the DSE technology is too low to enable a robust cost comparison. From these experiments, however, it is evident that the KOH buffer solution needs to be replenished periodically, leading to additional costs¹⁶.

Hausman et al. [14] looked into the often posited economic advantage of DSE, coming to the conclusion that it actually exhibits considerable disadvantages compared with ISE (water electrolysis / desalination), with minimal benefits. The authors state that it is less appealing than the two-step approach, as the capital and operational costs of water desalination are negligible compared with those of electrolysis for pure seawater [14]. Khan et al. [116] also compared DSE with ISE and found an insignificant increase in LCOH (<0.1 USD/kg H₂) and CO₂ emissions (< 0.1%) from a saltwater RO-PEM coupled process [116]. Yu et al. [118] and Jin et al. [20] have stated that this will change with time, as electrolyser costs are decreasing significantly. Therefore the share of water purification in the total costs of hydrogen may become more significant.

6.3 Land use comparison

In terms of land use, a seawater desalination plant that produces 100 million m³ of water per year occupies around 100 000 m² [101]. Smaller plants producing 10 000 m³ of water per year require between 4 500 m² and 6 100 m² [119]. However, it has to be considered that RO plants are commonly not optimised with regard to their footprint. Chico Moreno [120] surveyed companies offering more compact desalination units, the results are shown in **Table 4**. It should be noted that the output of the desalination units differs, with two step desalination likely to be the preferable version as it eliminates the need for further purification of the water.

¹⁶ USD > 800/t KOH [14]

Parameter	RO desalination (two step(^a))		RO desalination (one step(^b))
	Large scale	Small scale	Small scale
Distillate capacity (m³/d)	3800	100	100
Dimensions (I*w), (m)	15 x 10	7 x 4	2.8 x 1.7
Power installed (kW)	~700	~40	18.5
Investment (EUR millions)	3	0.3	-

Table 4 RO plant reference sizes and costs based on quotations from vendors [120].

(^a) This system produces high-purity water, ready for use in an electrolyser.

(^b) This system produces drinking-quality water.

Source: adapted from Chico Moreno [120], © 2024 Elsevier B.V. All rights reserved

To illustrate these numbers with an example, a 1 GW electrolyser producing 0.15 Mt H₂ per year, operating at full capacity, would require 3 million m³ per year of water, if a water consumption of 20 l/kg H₂ is assumed [115]. Three large-scale RO plants, as in **Table 4**, would be needed to supply water to a 1 GW electrolyser; these would occupy a space of around 500 m². Considering the 100 000 m² plot size estimated for an advanced 1 GW electrolyser [121], this space requirement does not appear to be a major factor.

However, for applications such as off-shore production of hydrogen, the additional space requirement for desalination may become more of an issue. Off-shore production of hydrogen is the focus of projects such as HOPE [122] and SEALHYFE [123], but there is no information regarding the size of the (planned) platforms. Zhang et al. [124] provide an estimate of the space requirements for offshore installations. The storage unit needs double the area of the production unit at 28.4 m²/MW. Based on the numbers provided, a 1 GW facility would need around 43 000 m², therefore the 500 m² space required for water desalination/purification is comparably insignificant.

Another advantage of DSE over ISE is supposedly related to the burden of the necessary infrastructure on land use and water transportation / availability. This has to be compared with the space needed for the electrolyser system. The additional space needed for water purification is less than 10% of the total area of the plant, and therefore is not a critical issue. For specific applications such as off-shore hydrogen production, a more integrated device might make sense, but will have to be accompanied by space-saving engineering solutions for components such as power electronics. Moreover, the low current densities (<0.5 A/cm²) of typical DSE prototype electrolysers could imply higher land use for a commercial-scale device.

Some papers claim there are potential benefits provided by better integration of the desalination and purification steps in DSE than in ISE. Better integration could potentially reduce the complexity of systems and provide operating or manufacturing benefits. However, since most of the systems are still on the laboratory scale, this benefit is difficult to assess based on the available literature.

6.4 Waste management comparison

Regarding waste management, namely the disposal of brine, at desalination plants the effluents are often disposed of by discharge into the sea. The brine can include chemical remnants from anti-scalants, anti-foaming agents and coagulants used in membrane-cleaning processes, potentially contaminating the highly saline effluent with toxins [125]. Efforts, such as dilution with seawater, are underway to minimise the impact on the marine ecosystem, but additional research may be needed. For DSE, the composition of the waste would depend on the approach, and may contain lye. There is no information yet on the composition and disposal of waste streams from DSE and the related potential environmental concerns.

7 Conclusions

- According to the literature reviewed, over time there has been an increasing interest in DSE in the scientific community, primarily in China. Europe has a lower (but probably increasing) share of publications. No commercial projects using DSE technologies for renewable hydrogen production are operating today. The technology is still at a very low TRL; the Clean Hydrogen JU call topic 'Development of innovative technologies for direct seawater electrolysis' (HORIZON-JTI-CLEANH2-2024-01-03¹⁷) gives TRL 2 as the starting point for projects. Most of the identified R&D activities are still on the laboratory scale, with the exception of one demonstration project run in China in 2023 [78].
- The research on DSE is very diverse and tackles a broad range of approaches, making it difficult to harmonise the evaluation of the results. It seems, however, that most of the focus is on the development of more suitable catalysts able to deal with impurities found in seawater. Little effort has been made to harmonise the testing protocols and to perform long durability tests. To a lesser extent, some studies worked on other designs, like the asymmetric feed of electrolytes or the use of unconventional membranes.
- The benefits of DSE should be assessed against the techno-economic and environmental performance of ISE. The proponents of DSE often claim that such systems could be cheaper and more energy efficient with a higher integration of the stacks within balance-of-plant components and a more compact system than ISE. A comparison of DSE with ISE is difficult as there is a lack of reliable and harmonised information regarding the performance of DSE. Our review does not show much evidence that new designs or materials for DSE, at least at the current stage of development, could offer a strong advantage over ISE in the near future, as the cost and energy penalty for purification of seawater is close to insignificant.

¹⁷ The high level of interest in Europe is evidenced by the 23 proposals received on this topic.

8 Recommendations

Identifying the most effective pathways from a technological, environmental and economic perspective

- 1. Most of the current research activities on DSE are happening on a laboratory scale, and it is not clear how this work will translate to the demonstration or commercial levels, or to full-scale DSE systems. Considering the extensive range of ideas, materials and designs that are being explored, the potential for upscaling should be considered when identifying promising future research avenues. Modelling activities could be used to virtually scale up newly developed materials or designs and assess the techno-economic performance. Low use of critical materials and any potential environmental benefits could be used as additional indicators. We recommend incorporating sustainability assessments into the investigation of these new technologies. The Clean Hydrogen JU could launch a study in order to help identify the best options. This could also be used to assess the success of any projects funded under the recent call topic HORIZON-JTI-CLEANH2-2024-01-03, as well as to help decide on future calls.
- 2. To enable the cost-effective and environmentally beneficial upscaling of systems using seawater, the performance of direct seawater systems must be assessed against a benchmark that uses desalination plants and conventional electrolysers. A more robust data collection exercise on the performance of ISE, from the cell level to full systems, would help in setting a proper benchmark for identifying the most promising DSE solutions. The performance should be evaluated in terms of efficiency (energy and resource use), safety and sustainability. For example, an issue needing further attention is the waste flow from both desalination and future DSE processes¹⁸, for example in order to allow brine management and the reintroduction of used seawater into the environment. This could be part of the study on water use planned by the Clean Hydrogen JU, included in the AWP 2024. Furthermore, in order to harmonise the comparison, we recommend the development of a clear terminology that is able to identify the differences between ISE and the multitude of DSE technologies to avoid confusion particularly for hybrid approaches.
- 3. The development of new designs of DSE with the capacity to collect and harvest valuable coproducts such as NaOH and other valuable raw materials (e.g. Li, Mg) could be useful [126]. As co-products can also be extracted from the brine of conventional desalination plants, it should be assessed whether DSE could provide an advantage in this regard. Similarly, although much of the research focuses on preventing the coproduction of chlorine species, exploring the niche application of multiproduct DSE may engender economic interest. Identifying industries capable of utilising both hydrogen and chlorine species could expedite the technology's scaling up.

¹⁸ In general, research on DSE should take waste management into account.

Increasing the efforts on material and components development

- In general, facilitating knowledge exchange between the research on DSE technology and that on other technologies utilising membranes, such as desalination plants, could be mutually beneficial. For example, the use of composite or bipolar membranes that can purify seawater before water splitting warrants further R&D. This research could also benefit desalination. In addition, little attention has been paid by researchers to the further development of polymeric ion exchange membranes for their use in DSE, which is a clear gap.
- 2. The development of components such as catalysts and membranes suited to harsher environments in the field of DSE remains of strategic interest. Further benefits can be explored through assessing the transferability of DSE technologies to the production of hydrogen using wastewater as feed. More R&D activities on such components could enable the drastic reduction of the impact of the large-scale deployment of renewable hydrogen production on freshwater resources.
- 3. Research on catalysts (and membranes) should be undertaken in harmonised conditions in order to avoid the effect of different compositions of electrolytes, or different electrolyser designs. This would enable effective comparisons between the multitudes of materials investigated. A study by Frisch et al. [59] proposed the use of a composition standard for saline water to enable comparison tests. However, it should be noted that this approach cannot take into account the variation of composition of natural seawater. This inability to compare results is a general unresolved challenge for DSE testing. Establishing a testing framework with well specified conditions and using a limited set of composition standards, is required to achieve repeatable, reliable and comparable test results.

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List of abbreviations and definitions

Abbreviation	Definition	
AEM	Anion exchange membrane	
AEMEL	Anion exchange membrane electrolysis	
AWE	Alkaline water electrolysis	
BCC	Basic cobalt carbonate	
BPM	Bipolar membrane	
CEM	Cation exchange membrane	
CER	Chlorine evolution reaction	
DSE	Direct seawater electrolysis	
FO	Forward osmosis	
HER	Hydrogen evolution reaction	
ISE	Indirect seawater electrolysis	
LCOH	Levelized cost of hydrogen	
LDH	Layered double hydroxide	
MD	Membrane distillation	
MEA	Membrane electrode assembly	
MEC	Microbial electrolysis cells	
MED	Multi-effect desalination	
MHCM	Metal hexacyanometallate	
MSF	Multistage flash desalination	
NF	Nickel foam	
OER	Oxygen evolution reaction	
PEM	Proton exchange membrane	
PEMEL	Proton exchange membrane electrolysis	
PGM	Platinum-group metals	
PRT	Pt, Ru and Ti	
PTFE	Polytetrafluoroethylene	
RED	Reverse electrodialysis	
RO	Reverse osmosis	
RR	Recovery ratio	
SDE	Self-dampening electrolyte	
SHE	Standard hydrogen electrode	
SOEL	Solid oxide electrolysis	
TFC	Thin film composite	
TRL	Technological readiness level	
UPW	Ultrapure water	

List of figures

Figure 1 Top 10 countres of origin of the authors of the papers identified by the Web of Science prompt 'seawater electrolysis AND hydrogen production'
Figure 2 Institution of origin of the papers identified by the Web of Science prompt
Figure 3 Number published per year, between 1992 and mid 2024, of the papers identified by the Web of Science prompt, and affiliation of authors
Figure 4 Number of papers tackling the 12 identified research focuses. HER, hydrogen evolution reaction; OER, oxygen evolution reaction
Figure 5 Graphic representation of possible issues at the cathode for HER in seawater. The green arrow is the HER, orange arrows are corrosion reactions and Mg(OH) ₂ as well as Pb represent possible depositions of impurities (oxides or metallic)
Figure 6 The Pourbaix diagram as elaborated by Dionigi et al. [15], from [12], the potential is calculated against a standard hydrogen electrode (SHE). The green line represents the thermodynamic equilibrium between water and oxygen. At electrode potentials higher than the green line, the OER process becomes thermodynamically possible. The red line shows the competing acidic oxidation of chloride to free gaseous chlorine. The black and pink lines mark the onset of the oxidation of chloride to hypochlorous acid, HClO, or hypochlorite, ClO ⁻ . The potential difference between the chloride chemistry and the water oxidation is the highest at 480 mV in alkaline media at a pH > 7.5 (light blue region), where chloride is oxidised to ClO ⁻ [12]
Figure 7 Schematic of AEMEL and possible degradation modes. (A) Asymmetric AEMEL: The concept of asymmetric feeding of the electrolyte is also further explored in section 4.3. (B) Possible electrolyser degradation mechanisms due to impurities [62]
Figure 8 Electrochemical seawater splitting based on reverse or forward osmosis, schematic from [73]. A: a forward-osmosis water-splitting cell and B: the membrane is placed between the two electrodes forming two separate chambers with the desalinated water drawn from the catholyte 29
Figure 9 Schematic depicting the liquid–gas–liquid phase transition-based migration mechanism of the water purification and migration process and its driving force [76]. SDE, self-dampening electrolyte
Figure 10 Schematics of membraneless electrolysers based on (left) flow-by electrodes and (right) flow-through electrodes. The inset in (right) shows a view of a mesh flow-through electrode evolving O ₂ as electrolyte passes through holes in the mesh, adapted from [79]
Figure 11 Classification of desalination technologies by working principle [94]
Figure 12 Global desalination capacity per type of technology in 2020 [95]. ED, electrodialysis; MED, multi-effect desalination; MSF, multistage flash desalination

List of tables

Table 1 Average concentration of impurities in seawater with around 3.5% salinity and their reactionsduring DSE. CER, chlorine evolution reaction; ppm, parts per million
Table 2Overview of the papers reviewed focusing on catalyst materials, tested in seawater. Buffersolutions were used to change the electrolyte pH. Usually the experiments were carried in a two- orthree- electrodes cell; when specified a membrane was also used. AEM, anion exchange membrane;NF, nickel foam; OEC, oxygen evolution catalyst; PBS, phosphate-buffered saline solution; SA, singleatom.18
Table 3 Overview of desalination technologies using data from various sources. MD, membrane distillation; MED, multi-effect desalination; MSF, multistage flash desalination
Table 4 RO plant reference sizes and costs based on quotations from vendors [120].

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