

Review article

Seawater as feedstock for large-scale green hydrogen production: A technical review from a desalination perspective

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ABSTRACT

This study examines the technical feasibility of using seawater as a feedstock for green hydrogen production, with a focus on system design and water treatment aspects. Both direct and indirect seawater splitting approaches are considered. Direct seawater electrolysis is excluded from further consideration due to unresolved challenges such as parasitic side reactions and electrode degradation. For make-up water generation, thermal desalination and seawater reverse osmosis (SWRO) were evaluated. Thermal desalination, though potentially powered by waste heat from electrolysis, was deemed impractical due to its dependence on the electrolyzer plant's heat management system, which complicates overall plant control. In contrast, SWRO operates as a standalone system and imposes minimal impact on hydrogen production costs through competing power consumption, making it the preferred option for large-scale applications. Alkaline Water Electrolysis (AWE) and Proton Exchange Membrane (PEM) electrolysis are identified as the only currently available industrial-scale electrolyzer technologies. A Balance of Plant analysis revealed key water treatment interfaces, including make-up water systems required for both technologies, and a loop purification system specific to PEM systems. A design study translated the identified requirements into practical plant configurations, providing a detailed evaluation of treatment options and implementation strategies. The study concluded with an outlook on future water-focused research, laying the groundwork for continued advancements in support of large-scale green hydrogen production.

1. Introduction

Human-induced climate change poses an existential threat to ecosystems, societies, and economies across the globe. Tackling this challenge demands immediate and coordinated efforts to transition away from fossil fuels and adopt sustainable energy solutions [1]. The Intergovernmental Panel on Climate Change's special report on the impacts of global warming of 1.5 °C emphasizes the critical need for global action to mitigate climate change and reduce reliance on fossil fuels [2]. This urgency has amplified the global search for sustainable energy alternatives to curb future carbon dioxide (CO₂) emissions, which are the primary driver of the greenhouse effect and hence a significant contributor to climate change [3–5].

Hydrogen (H₂), recognized as a clean energy carrier, has immense potential for storing and transporting renewable energy, making it a pivotal element in the transition to a sustainable energy future [6]. With an energy density of approximately 140 MJ/kg - more than twice that of

conventional fuels like gasoline or natural gas (50 MJ/kg) - hydrogen offers a pathway to reduced dependence on fossil fuels and significant reductions in greenhouse gas emissions [6–8]. Water electrolysis has thereby emerged as a key method for producing high-purity hydrogen (> 99.99 %) and oxygen (O₂) from water, making it a sustainable production option [9–11].

Currently, hydrogen consumption is largely confined to industrial sectors, such as the chemical and steel industries, where demand is steadily increasing [12]. The production is nowadays predominantly reliant on hydrocarbon-based processes, with steam methane reforming accounting for approximately 96 % of the global market [13,14]. However, the expansion of renewable energy sources, including photovoltaics and wind turbines, is expected to shift this trend towards green hydrogen [15]. In this context, electrolysis powered by renewable energy presents a viable decarbonization pathway, especially for countries with ambitious emission reduction targets. Yet, the current levelized cost of hydrogen (LCOH) can even reach 10 USD/kg or more,

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underscoring the need for technological improvements to reduce these expenses [16]. To align with the net-zero emissions (NZE) pathway, the International Energy Agency (IEA) has outlined projections for green hydrogen production from 2020 to 2050, estimating that 81 million tons (Mt) of production capacity is required by 2030, increasing to 322 Mt by 2050 to achieve these targets [17].

Advances in technology and large-scale deployment of renewables have driven down electricity generation costs by 70 % to 80 % over the past decade, positioning countries with high renewable energy capacities as potential leaders in developing large-scale green hydrogen hubs [12,18]. However, according to the IEA, LCOH is not solely dictated by declining electricity prices but is also heavily influenced by the pace and scale of deployment of electrolysis technologies. In the NZE Scenario, significant cost reductions in water electrolysis are anticipated with learning effects and economies of scale, expected to drive a 60 % decrease in capital expenditure (CAPEX) by 2030 compared to 2020 levels. Both effects combined are predicted to result in average LCOH of around 1.5 - 3.5 USD/kg by 2030 and 1.0 - 2.5 USD/kg by 2050, making

green hydrogen economically viable [17].

Recognizing the critical role of hydrogen in the green energy transition, over 60 countries had by 2024 already issued national hydrogen strategies to accelerate deployment and innovation [19]. As part of these efforts, Germany has set a target to install 10 GW of electrolyzers by 2030, supported by an expanded 1800 km pipeline network to replace natural gas in industry and transportation [20]. The USA is aiming for 10 Mt by 2030, scaling to 20 Mt by 2040 and 50 Mt by 2050 [20]. The UAE plans to produce 1.4 Mt by 2030, increasing to 15 Mt by 2050 through electrolysis, nuclear-powered systems, and natural gas with carbon capture [20]. Australia aims to produce 0.5 - 1.5 Mt by 2030, with export targets of 0.2 - 1.2 Mt by that year, and a total production target of 15 - 30 Mt by 2050 [21]. South Africa, leveraging domestic platinum resources, is targeting a production of 1 Mt by 2030, expanding to 4 Mt by 2050. Half of this production is destined for export, supported by USD 300 billion in investments and a focus on building 1 GW/a of PEM electrolyzer manufacturing capacity [19].

Despite its promise, water electrolysis presents challenges related to

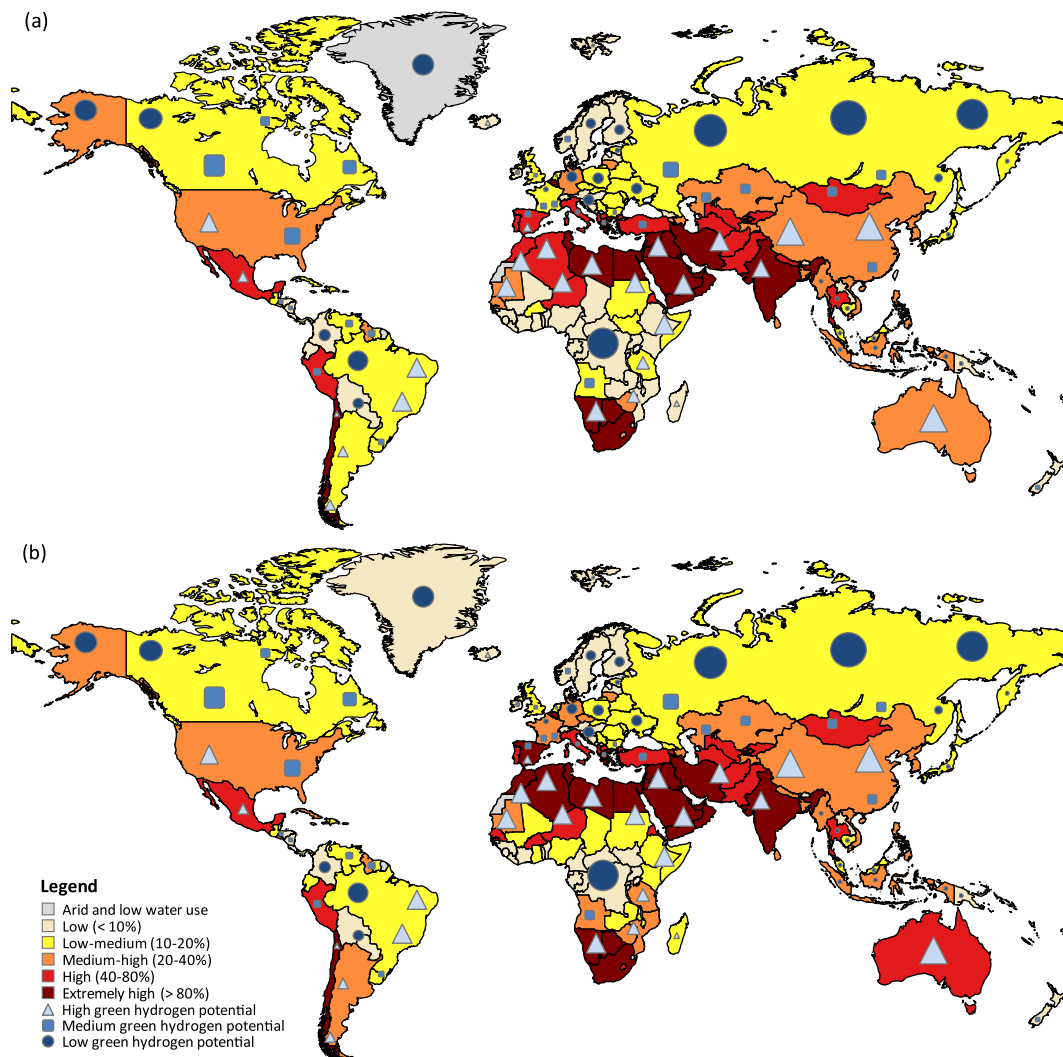


Fig. 1. Global water stress maps illustrating the demand-to-supply ratio for (a) 2023 and (b) projected 2050 conditions, highlighting growing water scarcity in regions with high solar and wind energy potential - critical areas for future green hydrogen production. Regions are classified by green hydrogen production potential: high (light-blue triangle), medium (blue square), and low (dark-blue circle), based on data from IEA 2024 [25], Levelised Cost of Hydrogen Maps, <https://www.iea.org/data-and-statistics/data-tools/levelised-cost-of-hydrogen-maps>, License: CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>). The size of each symbol reflects the size of the impacted area - larger symbols indicate larger regions with high renewable energy potential. Water stress projections are based on data from WRI 2024 [24], WRI's Aqueduct Water Risk Atlas, <https://www.wri.org/insights/highest-water-stressed-countries>, License: CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>).

freshwater availability [22]. Many regions with substantial renewable energy potential also experience water scarcity - a challenge projected to intensify in the future, as clearly illustrated by the water stress forecast for 2050 shown in Fig. 1 [12,23,24]. Taking this into account, the amount of water consumed in green hydrogen parks, either through direct production or stack cooling, can be an additional regional burden.

The theoretical minimum direct water demand through water electrolysis is defined by its stoichiometry at 9 kg H₂O per kg H₂. However, literature data suggest that actual water usage in practice could range up to 13 kg H₂O per kg H₂ due to factors such as evaporation, system leaks, water losses through the vented oxygen gas stream, and the need for equipment cleaning and flushing during maintenance [12,26]. Even though freshwater is often scarce in coastal regions, the unlimited availability of seawater, combined with abundant renewable energy potential makes these areas highly promising locations for sustainable hydrogen production [27]. In the case of Australia, for example, Geoscience Australia estimates that at 262,000 km², around 30 % of the areas considered highly suitable for green hydrogen production are located along its coastline [21].

Building on this context, this study examines the water aspects of green hydrogen production from seawater, adopting a technical perspective. It is organized into two sections with distinct objectives. The first section provides a critical review of the potential of seawater as a feedstock, evaluating suitable technologies and analyzing promising options within the framework of system design and key water treatment interfaces. This review establishes a detailed conceptual foundation and derives the key technical considerations that are further developed in the second section. In light of these findings, the second section presents a case study that develops specific plant designs aligned with the requirements identified in the first section. It offers a detailed assessment of treatment options and explores practical system implementations for large-scale applications.

The motivation for this investigation is driven by two main objectives: first, to clarify the role of water treatment-related interfaces, an area that has received relatively limited attention in the literature, and second, to define suitable treatment concepts for seawater as feedstock, while also highlighting ongoing research and future development potential.

2. Seawater as feedstock for green hydrogen production

Seawater as feedstock for hydrogen production can be utilized either through direct seawater splitting or indirectly via conventional water treatment followed by electrolysis. Direct splitting simplifies system design but is hindered by challenges such as catalyst degradation and ion interference. Conversely, indirect approaches involve pre-treatment to obtain high-purity water, facilitating efficient and reliable hydrogen production under stable operating conditions with established technologies.

2.1. Direct seawater splitting

Direct seawater splitting refers to the process of generating hydrogen directly from seawater through electrolysis without the need for enhanced pre-treatment or desalination. Seawater offers an abundant and geographically suitable resource, particularly in coastal regions where renewable energy sources are available [27]. However, the process faces significant challenges, primarily due to the competitive chlorine evolution reaction (CER) at the anode. CER, characterized by faster reaction kinetics (2-electron transfer) compared to the oxygen evolution reaction (OER) (4-electron transfer), is both thermodynamically and kinetically more favorable. The CER reaction, with a potential of 1.36 V vs. Standard Hydrogen Electrode (SHE) at pH = 0 and 0.89 V vs. SHE at pH = 14, is presented in Eq. (1) and 2 [28,29].



This competition cannot only reduce efficiency by causing corrosion and accelerating catalyst degradation but also generates hazardous chlorine gas, further complicating the feasibility and safety of direct seawater splitting [30,31].

Operating in alkaline conditions can suppress CER by favoring OER, as the theoretical potentials for CER and hypochlorite/chlorate formation are elevated in such environments. This suppression remains efficient despite a water oxidation catalyst exhibiting up to 480 mV overpotential under alkaline conditions (pH > 7.5), which serves as the design criterion for alkaline seawater electrolysis. However, at potentials exceeding 480 mV, hypochlorite formation remains a concern. These challenges are further exacerbated in industrial-scale electrolyzers, which typically operate at high current densities (> 0.5 A/cm²), leading to increased overpotentials that promote CER alongside OER [12,28]. Additionally, elevated pH promotes the deposition of hydroxides such as calcium hydroxide (Ca(OH)₂) and magnesium hydroxide (Mg(OH)₂) on the cathode, introducing further complications. These deposits, along with ions like magnesium (Mg²⁺), calcium (Ca²⁺), and sodium (Na⁺) in seawater, can reduce the catalytic activity and stability, blocking active sites on the electrode and reducing performance as well as operation efficiency [30,31].

Recent innovations, such as Lewis acid coatings and polyanion layers, have shown promise in improving reaction kinetics as well as in mitigating chlorine-related degradation, addressing key challenges associated with CER. However, despite these advancements, the technology remains immature, limiting its immediate application in commercial hydrogen production [12,28]. Further research is essential to overcome existing barriers and to establish direct seawater splitting as a viable and competitive technology. At present, no commercial projects employing this approach for renewable hydrogen production are in operation. Most ongoing research and development efforts remain at the laboratory scale, with the sole exception of a demonstration project launched in China in 2023 [32–34]. Given that this study focuses on industrial-scale green hydrogen production, direct seawater splitting is excluded from further consideration for the outlined reasons.

2.2. Indirect seawater splitting

Indirect seawater splitting describes hydrogen production through electrolysis while using desalinated seawater as feedstock [27]. The advantage of this approach is, that limitations, like scaling, fouling, or enhanced corrosion, caused by the complex composition of seawater are circumvented and stable operation conditions are generated [28]. Multiple desalination technologies have been historically employed, primarily for seawater desalination to produce drinking water. These technologies are generally categorized into thermal and membrane-based processes, each offering specific advantages and facing certain limitations [35].

Thermal methods such as multi-stage flash (MSF) and multi-effect distillation (MED) are well-established desalination technologies. MSF utilizes flash evaporation across multiple chambers and is often integrated with thermal power plants to capitalize on low pressure steam or waste heat. MED operates through progressive evaporation at lower pressures, requiring less external energy and offering reduced costs along with reduced scaling and corrosion issues [35]. Membrane distillation (MD), a hybrid thermal-membrane process, employs hydrophobic membranes for separation and excels in utilizing low-grade thermal energy, making it particularly suited for integration with low-temperature waste heat sources [36]. Thermal desalination methods generally produce higher-quality water than membrane-based technologies [35]. When feedwater is free of significant volatile organic contamination, as is usually the case for seawater according to MacKinnon (1979), the output water quality from thermal desalination can already be suitable for electrolyzer operation without further treatment

if manufacturer-specific requirements are met under all design conditions [37–40]. However, the dominant desalination process is membrane-based seawater reverse osmosis (SWRO), accounting for 70 % of the globally installed desalination capacity [41]. Its specific energy consumption (SEC) typically ranges from 3.0 to 5.0 kWh/m³, influenced by feedwater characteristics and system design [35,41]. Given that the typical permeate quality from SWRO is around 100 mg/L, depending on the chosen system configuration, additional post-treatment processes, such as ion exchange (IEX) or continuous electrodeionization (CEDI) are necessary to meet the high-purity water standards required for electrolysis, which are further discussed in **Chapter 5** [35]. An overview of the main desalination technologies discussed in this work is summarized in **Table 1**.

At first glance, the availability of waste heat from the electrolysis process offers a promising opportunity to lower the operation costs of the desalination process, as explored in several recent studies. However, most research still appears to focus predominantly on SWRO-based treatment. What often seems overlooked in this discussion is the practical engineering perspective rather than the theoretical potential alone.

Large-scale electrolyzer plants are designed as modular units to achieve capacities in the upper megawatt (MW) range [50–52]. The modular setup enables the heat management system to avoid centralization around a single large cooling tower, as is often the case with conventional power plants [53]. Using smaller cooling units not only supports the application of dry coolers, potentially reducing the water footprint, but also enhances system redundancy, thereby improving operational stability [53,54]. However, the selection of the most appropriate cooling method remains dependent on the specific site conditions of each project [53]. Centralizing and directly coupling the heat management system with the desalination system, on the other hand, consequently assumes steady-state operation. This means that any deviation from normal electrolyzer operation directly impacts water production, highlighting a critical limitation in practical operation. For instance, this issue will arise during wet-commissioning, plant start-up, or maintenance activities, when electrolyzers are filled with water for the first time or are not operating at full capacity and additional water for maintenance or flushing is needed exceeding the on-site water storage capacities. Furthermore, overall system control becomes more complex, as one subsystem directly influences the other.

When comparing, for example, a 1 gigawatt (GW) green hydrogen project utilizing AWE electrolyzers, a high-level rough calculation clearly demonstrates that the indirect production losses from the competing electricity consumption of the SWRO system are significantly less impactful than often indicated in literature. With an assumed SEC of 4.45 kWh/m³ for SWRO-based water treatment (4.0 kWh/m³ for double-pass SWRO [35]) with subsequent CEDI and IEX polishing (0.45 kWh/m³ [55,56]), the additional energy required to produce the expected 10.5 kg H₂O needed for the production of 1 kg H₂ amounts to just 0.047 kWh. This is approximately 0.09 % of the estimated total SEC for hydrogen electrolysis, which is 52.5 kWh/kg, assuming a beneficial electrolyzer efficiency of 75 % applied to the theoretical minimum of 39.4 kWh/kg [57]. The resulting indirect financial impact of production loss, based on an estimated LCOH of 5 USD/kg, is minimal at only 0.004 USD/kg. For a project of this size, with an average hydrogen production of 274,000 kg/d (at 60 % electrolyzer load), this equates to a total daily indirect hydrogen production loss through water treatment related power consumption of just 1220 USD - insignificant compared to the estimated daily average revenue of 1370,000 USD.

This analysis highlights that the electrical energy demand associated with SWRO-based water treatment is minimal compared to thermal desalination, especially when considering the additional complexities of integrating thermal processes into the system. Moreover, the results are so clear that even significant changes in the main parameters do not alter the obtained order of magnitude. This remains valid despite applying the most favorable boundary conditions for the analysis, excluding the electrical consumption for thermal desalination technologies, which is also in a range of 1.5 - 2.0 kWh/m³ for MED [35], 3.0 - 4.0 kWh/m³ for MSF [35], and 1.5 - 3.7 kWh/m³ for MD [58]. As a consequence, the actual difference is even smaller. Given the minor production loss and the significant disparity in CAPEX between the AWE electrolyzers (around 500 mUSD [59,60]) and the required SWRO-EDI-IEX system with a production capacity of 4800 m³/d (around 12.0 mUSD, as indicated by a CAPEX estimate based on in-house supplier quotations conducted for this study), it seems unlikely that such integration would be considered technically viable or meaningful during risk assessment in the project planning stage. This conclusion is further reinforced by the fact that, in this capacity range, SWRO also represents the most cost-effective option in terms of CAPEX, as summarized in **Table 1**. The focus of this study will therefore be placed on SWRO-based water treatment, and thermal desalination will not be further discussed.

3. Fundamentals of water electrolysis technologies

Green hydrogen can be produced through various technologies, including water electrolysis, microbial electrolysis, and solar-driven processes [61]. Among these, electrocatalytic water splitting powered by renewable energy is one of the most promising methods for sustainable hydrogen production. This approach, which has a minimal carbon footprint, utilizes various types of electrolyzers, mainly including Alkaline Water Electrolysis (AWE), Proton Exchange Membrane (PEM) electrolysis, Solid Oxide Electrolysis (SOEC), and Anion Exchange Membrane (AEM) electrolysis.

AEM and SOEC were excluded from further consideration at this stage due to their early development phase, which does not align with the industrial-scale production focus of this study [61–64]. However, key research challenges underscore their potential for future viability, provided that competitive solutions can be developed. SOEC, for example, offers the highest efficiencies but requires elevated operating temperatures of approximately 700–900 °C, leading to material degradation and thermal cycling stress. Ongoing research aims to enhance ceramic electrolyte stability, develop protective coatings to mitigate electrode degradation, and optimize stack designs to improve durability and reduce overall system costs [65–68]. Similarly, AEM technology integrates the cost advantages of AWE with the operational flexibility of PEM but remains in the early stages of development due to challenges such as low membrane conductivity, limited durability, and catalyst instability. Advancements in high-conductivity, long-lasting anion exchange membranes, non-precious metal catalysts, and alkaline-stable electrodes are critical for achieving commercial viability [69–71].

A general process flow diagram for AWE and PEM, illustrating system inputs and outputs with a focus on water treatment-related interfaces and subsystem boundaries, including electricity, seawater, brine, make-up water, hydrogen, and oxygen, is shown in **Fig. 2**.

AWE electrolysis is currently the most mature technology but has relatively low efficiency, driving interest in alternative solutions. PEM, SOEC, and AEM electrolyzers offer higher efficiency, greater operational

Table 1
Cost comparison of desalination technologies with production capacities ≤ 20,000 m³/d.

Technology	Product TDS in mg/L	CAPEX in USD/(m ³ /d)	OPEX in USD/m ³	LCOW in USD/m ³	Polishing required	Sources
Double pass SWRO	< 100	1700 – 2700	0.5 - 1.0	1.1 - 1.9	Yes	[42–47]
MED	< 10	2100 - 2800	0.6 - 1.2	1.3 - 2.0	For target conductivities < 5 μS/cm	[45–49]
MSF	< 10	2700 - 3400	1.0 - 1.5	1.9 - 2.5	For target conductivities < 5 μS/cm	[45–47]

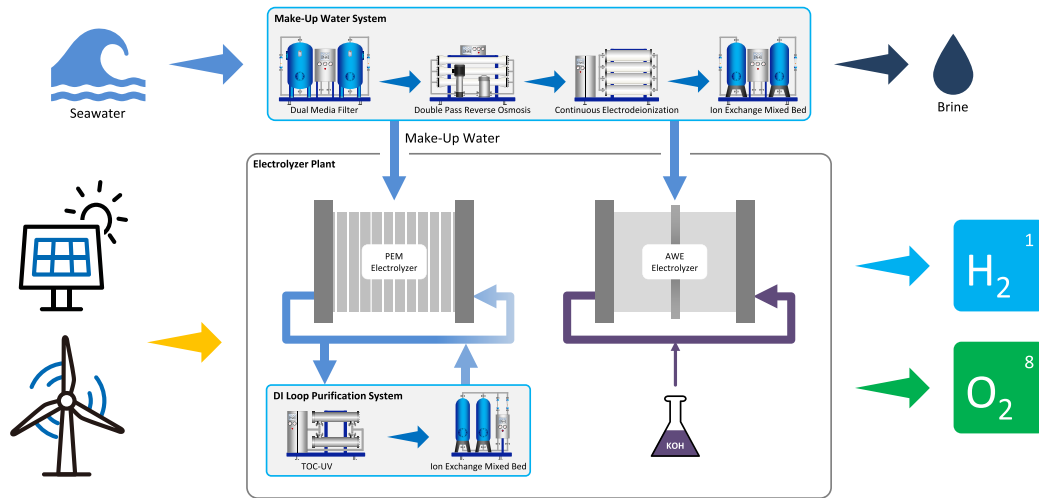


Fig. 2. General process flow diagram for AWE and PEM electrolysis systems, illustrating plant inputs and outputs across subsystem boundaries with a focus on water treatment-related interfaces, including electricity, seawater, brine, make-up water, hydrogen, and oxygen.

flexibility, and a more compact design but either rely on costly materials, increasing capital expenses, or face unresolved research and development challenges, as outlined above [61].

Recent efforts to make green hydrogen competitive focus mostly on advancing both AWE and PEM electrolysis. A key objective is to reduce CAPEX by using more cost-effective materials and components, as well as lowering OPEX, primarily through reduced energy consumption and electricity costs [19,72–74]. The global push for large-scale electrolysis has raised new considerations around its impact on worldwide energy dynamics and the equilibrium between countries as they adopt these technologies within their energy policies [75,76]. A particular emphasis is placed on managing critical raw materials, which could significantly affect production costs, especially for technologies that depend on rare or geographically limited resources like iridium for PEM electrolyzers [76–78].

3.1. Alkaline water electrolysis

AWE, discovered by Troostwijk and Diemann in 1789, is a well-established and mature technology widely used for hydrogen production, particularly on a large commercial scale [70,79]. This process typically operates at low to moderate temperatures, between 60 °C and 90 °C [59,70]. It usually utilizes an alkaline electrolyte solution of potassium hydroxide (KOH) at a concentration of typically 20 - 30 % to ensure an adequate supply of hydroxide ions (OH^-), which serve as the primary charge carriers in the electrolyte (see Fig. 3). This enables efficient ionic conductivity, facilitating the transfer of charge between electrodes while maintaining chemical stability to optimize hydrogen and oxygen production [80].

The electrolysis setup consists of two electrodes, typically made from nickel-based materials. The anode is often enhanced with nickel oxides or alloys, while the cathode may include cobalt or other catalytic coatings for improved performance. They are separated by a porous diaphragm, made of materials such as asbestos, ceramic oxides or synthetic polymers, which prevents the mixing of hydrogen and oxygen gases to ensure safety and maintain efficiency [57,70,79,81]. OH^- ions generated during the process pass through this diaphragm to facilitate hydrogen production at the cathode and oxygen generation at the anode [82].

AWE has several advantages, including low OPEX, moderate energy efficiency of around 62 to 82 %, high service life of typically up to 90,000 operating hours, and the ability to produce the greatest nominal outputs (> 100 MW) operating without expensive catalysts [57,59,60]. Further, AWE is the most cost-effective electrolyzer type on the market in terms of CAPEX. As for other electrolyzers, its current CAPEX varies

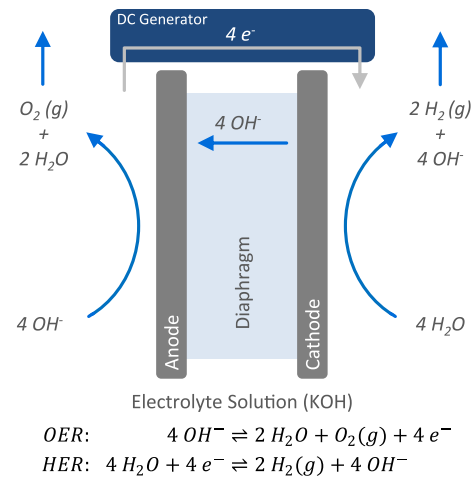


Fig. 3. Functional principle of AWE electrolysis, illustration adapted from Wang et al. 2022 [79], *PEM water electrolysis for hydrogen production: fundamentals, advances, and prospects*, <https://doi.org/10.1007/s43979-022-00022-8>, License: CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>), and modified based on [57,70].

thereby significantly, largely depending on the system's installed production capacity, with values ranging from approximately 500 to 1400 USD/kW of installed capacity [59,60].

However, several challenges persist. The technology operates, for example, compared to other electrolyzers at relatively low current densities (200 to 400 mA/cm^2) [83,84]. This is the result of ohmic losses across the electrolyte and the diaphragm. Beyond that, the technology is prone to electrode corrosion [57,85]. Also worth mentioning is that AWE electrolyzers exhibit slower operational dynamics than, for example PEM or SOEC, requiring 1–10 min for shutdown and up to 50 min for cold start-up. Also, their load range is more limited, operating typically between 20 % and 100 % of nominal load, with ramp rates from 0.2 % to 20 % per second [5]. This issue arises from the risk of hydrogen and oxygen mixing, which can create explosion hazards. Prolonged operation under such conditions can disrupt the pressure balance between the anode and cathode sides, leading to hydrogen buildup through gas diffusion across the diaphragm. This buildup can potentially exceed the lower explosion limit (LEL) of 4 % hydrogen in oxygen, posing a significant safety risk and reduces production efficiency as well [5,6]. Since the gases produced at both, the cathode and

anode, can easily diffuse through the porous diaphragm, hydrogen purity levels are limited to approximately 99.5 % to 99.9 %. Therefore, purification using a deoxygenation reactor as well as gas dryers is necessary to remove oxygen and water vapor traces, increasing hydrogen purity to levels exceeding 99.999 % when higher purity is required [86]. In addition, the liquid electrolyte restricts the system's ability to operate at high pressures, which affects the overall compactness and performance of the electrolyzer stack [6].

3.2. Proton exchange membrane electrolysis

PEM electrolysis, developed by General Electric in the 1960s, introduced a new approach to hydrogen production by using a perfluorosulfonated acid (PFSA) membrane (e.g., Nafion) as a solid electrolyte [87]. Unlike alkaline electrolysis, which relies on a liquid electrolyte, this solid electrolyte design offers a simpler system with enhanced performance [79]. The membrane serves as both, electrolyte and gas separator, allowing only deionized (DI) water without additives to be injected into the cell during the electrolysis process [70,81]. The solid electrolyte facilitates proton conduction (see Fig. 4), enabling the migration of hydrogen ions (H^+) across the membrane to form hydrogen molecules on the cathode side [62,64].

PEM electrolysis has several advantages, such as high current density of around 0.6 to 2.0 A/cm², greater energy efficiency than AWE (67 % to 82 %), low gas permeability resulting in hydrogen purity of ≥ 99.999 %, and a wide operating temperature range of 50 to 80 °C [59,70,79]. The reaction kinetics in PEM cells are more rapid than in alkaline electrolyzers due to the acidic nature of the electrolyte and the metallic electrode surfaces, making the process safer and allowing for high-pressure operation at typically between 30 and 80 bar, particularly on the cathode side. Additionally, PEM electrolyzers feature a compact design and can operate across a wide load range with a high service life of approximately 60,000 operating hours [59,70,79]. They enable highly dynamic operation, including rapid shutdown within seconds and start-up times ranging from 1 s to 5 min, depending on temperature conditions. Furthermore, PEM electrolyzers support a load range from 0 % to 160 % of nominal load, with ramp rates of up to 100 % per second [5].

Despite these benefits, PEM electrolysis faces challenges, particularly in terms of cost, as it relies on precious metal catalysts like platinum (Pt) and iridium oxide (IrO₂) to withstand the acidic environment [70,76,88]. Iridium, one of the rarest elements in the Earth's crust, has become

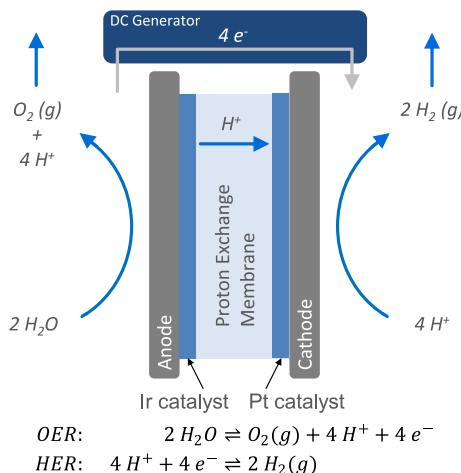


Fig. 4. Functional principle of PEM electrolysis, illustration adapted from Wang et al. 2022 [79], *PEM water electrolysis for hydrogen production: fundamentals, advances, and prospects*, <https://doi.org/10.1007/s43979-022-00022-8>, License: CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>), and modified based on [57,70].

a significant cost bottleneck for PEM technology, with its price increasing by 400 % compared to the average price between 2015 and 2020. As a result, the CAPEX for PEM electrolyzers remains high, ranging from 1100 to 1800 USD/kW of installed capacity, depending on the system's scale [60,76]. Scaling up PEM electrolyzers stacks into the multi-MW range is also challenging, requiring extensive analysis to validate the technology's performance and durability at these capacities [81]. The findings of the above outlined review for AWE and PEM are summarized in Table 2.

4. Balance of plant for AWE and PEM electrolyzers

To identify water treatment-related interfaces for AWE and PEM electrolyzers, a detailed examination of the Balance of Plant (BoP) for both systems was conducted. This analysis was deemed crucial to accurately describe the prevailing operating conditions, as well as the specific requirements and challenges associated with water purification and management for each electrolyzer technology.

The BoP, an overarching term for all auxiliary subsystems supporting the electrolyzer stack, is essential for ensuring performance, reliability, and safety by addressing key aspects such as water supply, gas management, thermal regulation, and power supply [89]. As outlined by various studies [52,89–92], the BoP can generally be categorized into the following subsystems:

- **Control Subsystem (CS):** Monitors and controls parameters such as temperature, pressure, gas purity, leakage detection, and flow rates automatically through actuators, ensuring safe and efficient operation. All other subsystems are controlled through the control subsystem.
- **Power Supply Subsystem (PSS):** Supplies and conditions the electrical energy required for electrolysis, including rectifiers, inverters, and protective devices.
- **Gas Management Subsystem (GMS):** Handles separation, purification, drying, and compression of hydrogen and/or oxygen gases. Gas-liquid separators and storage units are integral parts of this subsystem.
- **Water Management Subsystem (WMS):** Supplies DI water to the electrolyzer, ensuring purity and circulation. It also includes components for water purification, recirculation, and pressure regulation.
- **Heat Management Subsystem (HMS):** Regulates the electrolyzer stack temperature to maintain optimal operating conditions using cooling loops and heat exchangers.

Table 2

Comparison of typical characteristics of AWE and PEM electrolyzers.

Specification	AWE	PEM
Operating conditions		
Cell temperature in °C	60 - 90	50 - 80
Cell pressure in bar	1 - 30	30 - 80
Current density in A/cm ²	0.2 - 0.4	0.6 - 2.0
Cell voltage in V	1.8 - 2.4	1.8 - 2.2
Voltage Efficiency in %	62 - 82	67 - 82
Stack lifetime in h	< 90,000	< 60,000
Hydrogen purity in %	99.5 - 99.9	≥ 99.999
Process design		
Electrolyte	20 - 30 % KOH	PFSA
Charge carrier	OH ⁻	H ⁺
Separator	Asbestos, NiO, ZrO ₂	PFSA (e.g., Nafion)
Cathode	Ni, Ni-Mo alloys	Pt, Pt-Pd
Anode	Ni, Ni-Co alloys	RuO ₂ , IrO ₂
Economic aspects		
Technology maturity	Mature	Commercial
Capital costs in USD/kW _{el}	500 - 1400	1100 - 1800

Abbreviations: NiO = Nickel Oxide, ZrO₂ = Zirconium Dioxide, Ni = Nickel, Ni-Mo = Nickel-Molybdenum alloy, Pt-Pd = Platinum-Palladium alloy, Ni-Co = Nickel-Cobalt alloy, RuO₂ = Ruthenium Dioxide

The AWE and PEM system designs discussed in this chapter are based on commercially available large-scale modular systems, where scaling up is achieved by connecting multiple modules to reach the desired capacity [52]. The sizing and redundancy of shared BoP systems are determined by balancing CAPEX, system flexibility, and downtime, as in other industrial facilities. Larger equipment with less redundancy can minimize CAPEX through economics of scale but may elevate the risk of prolonged downtime. In contrast, smaller, more redundant equipment enhances system flexibility and reduces downtime but comes with higher installation costs. These design choices are ultimately guided by project-specific requirements and site conditions, including the expected electrolyzer load.

Suppliers offering modular large-scale AWE systems include Thyssenkrupp Nucera with their Scalum system, providing 20 MW per module [51]; McPhy with the McLyzer 3200–30 system, delivering 16 MW per module [93]; and Asahi Kasei with the Aqualyzer system, offering 10 MW per module [94]. In contrast, for PEM systems, smaller stack sizes lead to stack array designs with a greater number of individual stacks per module. Notable examples include Accelera's HyLYZER 5000 system, which features ten 2.5 MW stacks for a total capacity of 25 MW per module [95]; Siemens' Silyzer 300 system, delivering 17.5 MW per module using 24 stacks [96]; Nel's PSM Series with eight 1.25 MW stacks for a total of 10 MW per module [50]; and ITM's Poseidon system, which combines 15 stacks to achieve 20 MW [97].

Examining realized and upcoming projects for both technologies reveals the same system capacity trend. According to the IEA Hydrogen Production Projects Database [98], the largest realized AWE project so far is the Sinopec-Kuqa project in China, with a capacity of 260 MW, completed in 2023, followed by the Ningxia Solar Hydrogen Project, Phase 2 (150 MW, completed in 2021, China). In contrast, the largest operational PEM electrolyzer to date is a 40 MW plant in Camden County, USA, which became operational in 2024, with most other PEM projects in the 20 MW range. Notable upcoming AWE projects include the NEOM Green Hydrogen Project in Saudi Arabia (2.2 GW, expected online in 2026), the Greenko ZeroC project in India (1.3 GW, expected online in 2027), and the Siziwang Banner project in China (1 GW). Meanwhile, the largest PEM projects under construction include Normand'Hy in France (200 MW, online in 2026), GET H2 Nukleus Phase 2 in Germany (200 MW, online in 2027), and EWE's Clean Hydrogen Coastline in Germany (280 MW, online in 2028).

This comparison underscores the dominance of AWE systems in terms of scale, while PEM projects, though smaller, are steadily advancing in capacity to meet growing market demands. It seems only a matter of time before projects in the GW range become a reality for both technologies.

4.1. Power supply and control subsystem

The PSS for green hydrogen production through AWE and PEM electrolysis operates on a similar principle, as both rely on renewable energy sources. An AC/DC rectifier plays a critical role in this by converting the supplied variable alternating current (AC) from these sources into a stable direct current (DC). This conversion is essential for electrolysis because it provides a unidirectional flow of electrons necessary to drive consistent oxidation and reduction reactions at the electrodes. The decomposition of water begins once a DC voltage higher than the thermoneutral potential is applied to the electrodes [99].

While AC rectification is an efficient process, larger systems require air or liquid cooling to prevent overheating [52]. The primary sources of energy dissipation include ohmic losses in electronic components, ionic conductors, and charge transfer resistance. The stack voltage, determined by the number of cells and their nominal voltage, typically reaches several hundred volts. Over time, cell degradation increases voltage demands, necessitating rectifiers designed to accommodate both beginning-of-life (BOL) and end-of-life (EOL) voltage ranges. The stack

current, influenced by the cell area and current density, can reach up to 30,000 A for industrial-scale systems [100]. It corresponds directly to the volume of hydrogen produced [101].

Since grid stability cannot always be guaranteed when using renewable energy sources, filters are integrated into the PSS design to manage harmonic distortion. Nevertheless, some residual reactive power can remain, requiring compensation measures such as static synchronous compensators [100]. The system's connection to the electrical grid must align with the plant's maximum capacity. Electrolysis plants with single-digit megawatt capacities are typically connected to mid-voltage grids (20–30 kV), while a 100 MW plant is generally connected to a high-voltage grid (110 kV). For plants with capacities of 1 GW or more, connection to the transmission grid (380 kV) is standard. Despite these varying grid connection levels, rectifiers operate with approximately 0.4 kV at low voltages. They are typically powered through individual low-voltage transformers [100]. Depending on regional standards, the actual voltage transformation levels may vary slightly.

Multi-stack configurations with individual power supplies alongside shared BoP systems are preferred for large-scale systems because they offer advantages during maintenance, allowing the isolation of a single electrolyze stack without disrupting ongoing production while reducing CAPEX at the same time. Parallel wiring further supports flexibility by enabling the replacement of individual stacks with units of equivalent impedance [52]. Fig. 5 presents a simplified PSS for a 1 GW electrolyzer plant, consisting of ten electrolyzer arrays, each with an installed capacity of 100 MW.

Similarly, the CS for both technologies is designed in a comparable manner, tasked with monitoring, regulating, and ensuring the safe and efficient operation of the entire process. It typically incorporates sensors to measure critical parameters such as temperature, pressure, flow rates, gas purity, and water quality [89–91]. Data from these sensors is processed by controllers in order to automate operation and to adjust variables like current density, water flow rate, or system pressure as needed.

Another crucial function of the CS is managing the explosion risks inherent to hydrogen production. This includes integrating gas leak detectors, gas purity measurement in the form of oxygen to hydrogen (OTH) as well as hydrogen to oxygen (HTO), pressure monitoring, and safety interlocks to prevent dangerous hydrogen and oxygen mixtures.

4.2. Gas management subsystem

The first differences in the BoP between AWE and PEM systems are represented in the GMS. The GMS is responsible for handling the produced oxygen as well as hydrogen streams. The oxygen subsystem for both electrolyzer types is more or less equivalently designed, as shown in Fig. 6 as well as Fig. 8 for AWE and Fig. 7 as well as Fig. 9 for PEM. It follows a straightforward configuration, consisting of a gas-liquid separator (GL300), a gas chiller (HE300), a demister (DM300), and a downstream control valve (CV300). The gas-liquid separator removes entrained liquid from the oxygen stream, while the demister captures any remaining fine mist or droplets. The downstream control valve maintains the required pressure for operation of the upstream processes. After undergoing these steps, the oxygen, along with minor traces of water vapor, is usually vented to the environment [89,92,99,100,102].

Hydrogen purity requirements vary depending on the end-user case. Fuel cells, for example, demand according to ISO 14,687–2 a purity of $\geq 99.97\%$, alongside stringent impurity limits such as total non-hydrogen gases (≤ 300 ppm), nitrogen (≤ 300 ppm), CO_2 (≤ 2.0 ppm), water (≤ 5.0 ppm), and oxygen (≤ 5.0 ppm). For ammonia and methanol synthesis, less stringent hydrogen purity requirements apply. However, both water and oxygen must still be limited, as they can negatively impact the catalysts used in the methanation and the Haber-Bosch process [102,103].

As already referenced in Chapter 3, PEM electrolyzers often produce

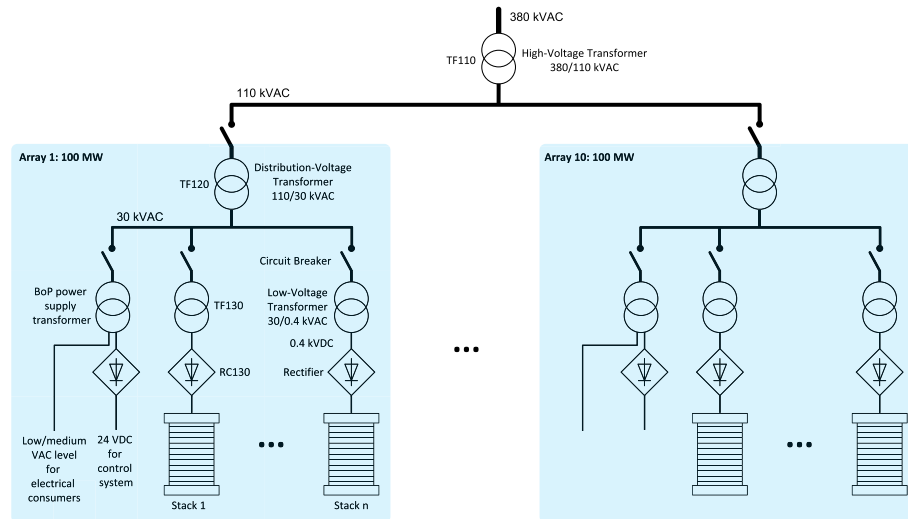


Fig. 5. Simplified PSS for a 1 GW electrolyzer plant with ten 100 MW electrolyzer arrays, including key components such as a high-voltage transformer (TF110), distribution voltage transformers (TF120), low-voltage transformers (TF130), and rectifiers (RC130). Reproduced and adapted with permission from [100], copyright: Fraunhofer Institute for Solar Energy Systems ISE, modified based on [52].

hydrogen at purities that inherently meet or exceed these thresholds ($\geq 99.999\%$), including the stringent fuel cell criteria, which minimizes the need for sophisticated downstream purification systems compared to AWE systems, which usually only obtain a purity between 99.5% and 99.9% . Hence, the hydrogen purification subsystem for AWE electrolyzers is naturally more complex [89,90,104].

As for the PEM systems, the process begins with a gas-liquid separator (GL400), followed by a gas chiller and a demister (DM400) to eliminate remaining moisture. Subsequently, a scrubber (SC400) is employed to remove residual fine aerosols and KOH mist by contacting the gas stream with either make-up water or diluted electrolyte as the scrubbing liquid, depending on the system configuration. Downstream of the scrubber, a gas holder (GH400) is positioned at the plant level. It serves as a buffer storage vessel, stabilizing hydrogen flow and pressure to ensure a consistent supply to the subsequent purification processes. It

also decouples the electrolyzer to a certain extent from downstream stages, enhancing operational flexibility and safety by temporarily storing hydrogen and mitigating pressure fluctuations [100].

AWE systems typically operate at lower pressure levels, as the anode and cathode sides are not decoupled like in PEM electrolyzers but are instead connected via a diaphragm [57,70]. To address this, a typically air-cooled compressor (CO400) is installed between the gas holder and the deoxidation reactor. By creating a higher pressure level, the compressor improves reaction efficiency during the deoxidation process and prepares the hydrogen for meeting the interface requirements of the hydrogen compression and storage unit located further downstream, which is beyond the scope of this study. Holst et al. [100] concluded in their work that 4 x four-stage compressor systems, each rated at 650 kW, would be required to elevate the pressure from 1 bar to 30 bar for a 100 MW system. This approach with several compressors working in parallel

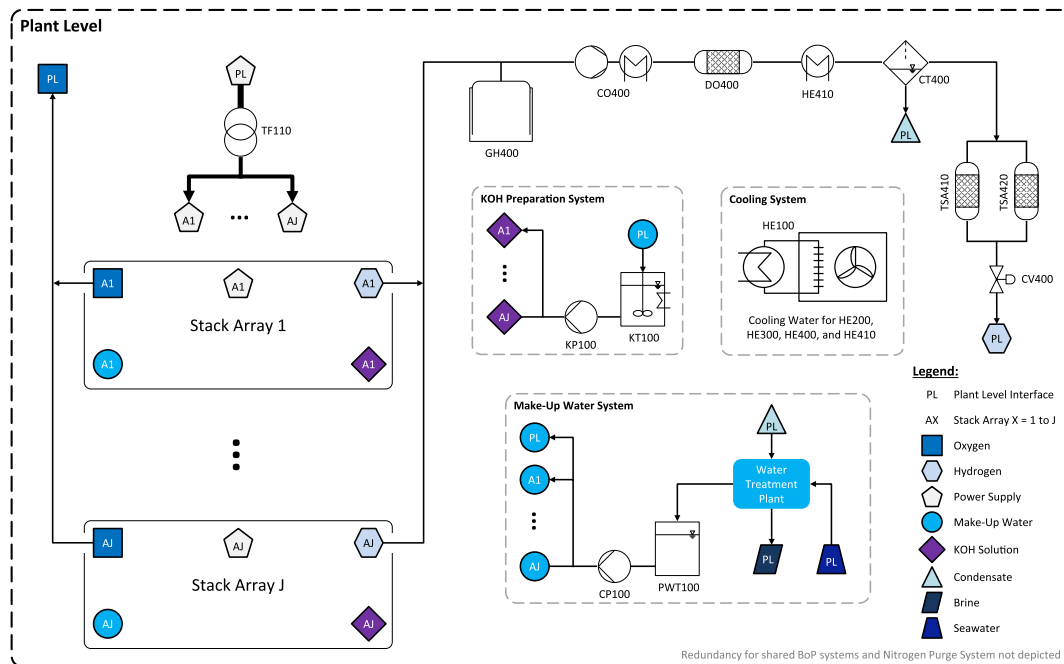


Fig. 6. Typical plant level BoP diagram of an AWE electrolyzer system including a make-up water system, KOH preparation system, cooling system, power supply system, hydrogen purification system, and various electrolyzer stack arrays. Schematic redrawn and summarized based on [89,90,100].

was chosen to account for the limited part-load performance of mechanical compressors during fluctuating electrolyzer loads.

The subsequent treatment steps are equivalent for both systems. To remove trace oxygen, the deoxidation unit (DO400) uses a catalyst, such as palladium or platinum, to convert oxygen into water via reaction with hydrogen [52,100]. A gas chiller (HE410) and a condensate trap (CT400) then remove condensate from the saturated gas stream [102]. Further downstream, temperature swing adsorption (TSA410 and TSA420) or pressure swing adsorption (PSA) is applied in at least two adsorption-regeneration columns filled with solid desiccants such as alumina, silica gel, or molecular sieves as the final treatment step [102]. For regeneration, the column is heated using an electric heater to desorb water and gas traces from the adsorption material. In the case of PSA, regeneration is achieved by reducing the pressure in the column to release the adsorbed impurities. TSA is usually preferred over PSA for its superior ability to effectively remove water vapor and its higher regeneration efficiency. During regeneration, the column is purged with a small amount of dried product gas to flush out the desorbed impurities, restoring the column for the next adsorption cycle [52,100]. A downstream control valve (CV400) maintains the required pressure level for both setups.

4.3. Water management subsystem

Water is the primary reactant in hydrogen production via electrolysis. However, impurities in the feed water can poison and deactivate catalysts, degrade membranes, or clog diaphragms, leading to significantly increased cell voltages and, consequently, to reduced efficiency [105]. To mitigate these degrading effects on electrolysis cells, both AWE and PEM systems require high-purity feed water as a preventative measure. As a result, all commercially available electrolysis systems are equipped with water purification units to produce DI water as make-up water for the process [52,99].

The overall cost of water treatment is heavily influenced by factors such as the quality of the feed water source, transportation distance, and potential additional costs for the management of wastewater streams [26]. In large-scale electrolysis systems, such as those examined in this study, the water purification system typically accounts for less than 1 %

to 2 % of the total project cost, as outlined in **Chapter 2.2**. Furthermore, this cost share decreases as the capacity of the electrolyzer system increases.

For both technologies, the WMS begins with the make-up water system, which removes impurities such as total dissolved solids (TDS), total organic carbon (TOC), and total suspended solids (TSS) from seawater, producing purified water of sufficient quality for the electrolysis process. In addition to seawater, condensate streams from sources such as the hydrogen purification system are also recycled within this setup in order to reduce the water footprint [89,100]. Design considerations for the make-up water system are discussed in greater detail in **Chapter 6**. The DI water is then stored in the pure water tank (PWT100), which serves as a reservoir to ensure a consistent and stable water supply. From this tank, the make-up water is distributed to the various stack arrays using distribution pumps (CP100).

For **AWE systems**, there are multiple interfaces at stack array level, the water is simultaneously introduced into the lye circulation loop and utilized in the scrubber (SC400) as scrubbing liquid. Additionally, it is supplied to the KOH preparation system, where it is used to dissolve solid KOH flakes in the KOH preparation tank (KT100), creating a solution with a higher concentration than that in the lye circulation loop. This concentrated solution compensates for minor KOH losses during operation by being dosed with a KOH dosing pump (KP100) into the lye circulation loop at the stack level, ensuring the desired KOH concentration of 20 - 30 % is maintained. The dosing point is located upstream of the lye circulation pump (see Fig. 8) to ensure proper mixing. The concentration is typically monitored via conductivity measurement downstream of the lye circulation pump [106]. It is critical to position the measurement device in a way that prevents bubble formation around the probes, as this could disrupt the accuracy of the measurement. The KOH preparation system is also used to fill the lye recirculation loop for the first time during commissioning [100].

The diluted electrolyte solution from the scrubber is also fed into the lye circulation loop. The lye is circulated by the lye circulation pump (CP200), which passes it through a heat exchanger (HE200) for temperature regulation, maintaining an operating temperature usually in a range between 60 °C and 90 °C. Then, the lye flows through a lye filter (LF200) to remove impurities in the form of solid particles [90]. This

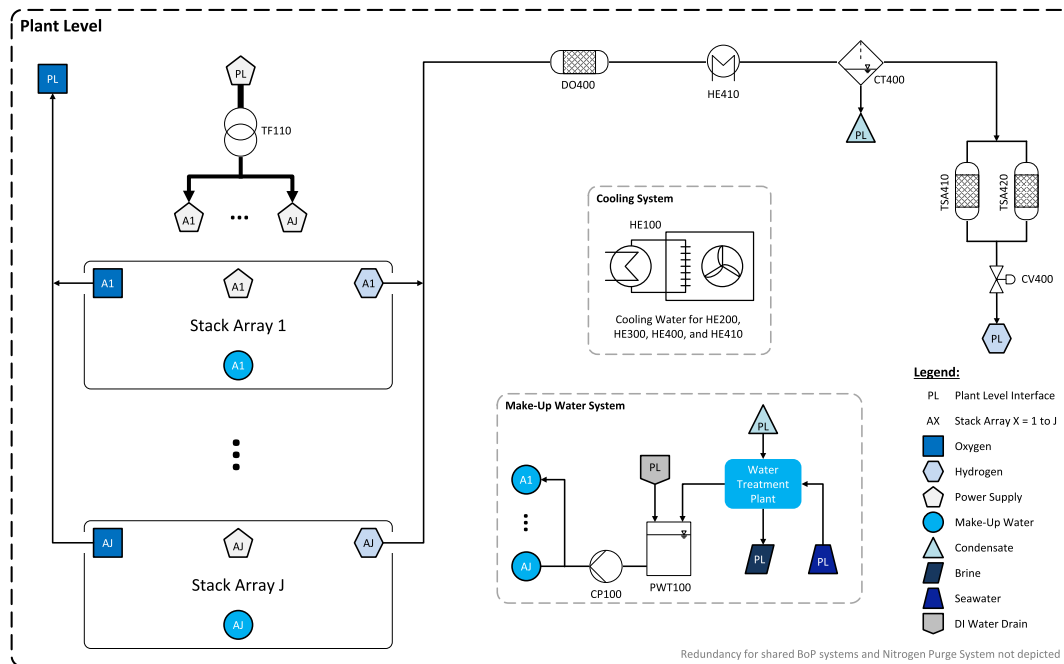


Fig. 7. Typical plant level BoP diagram of a PEM electrolyzer system including a make-up water system, cooling system, power supply system, hydrogen purification system, and various electrolyzer stack arrays. Schematic redrawn and summarized based on [91,92,99,100].

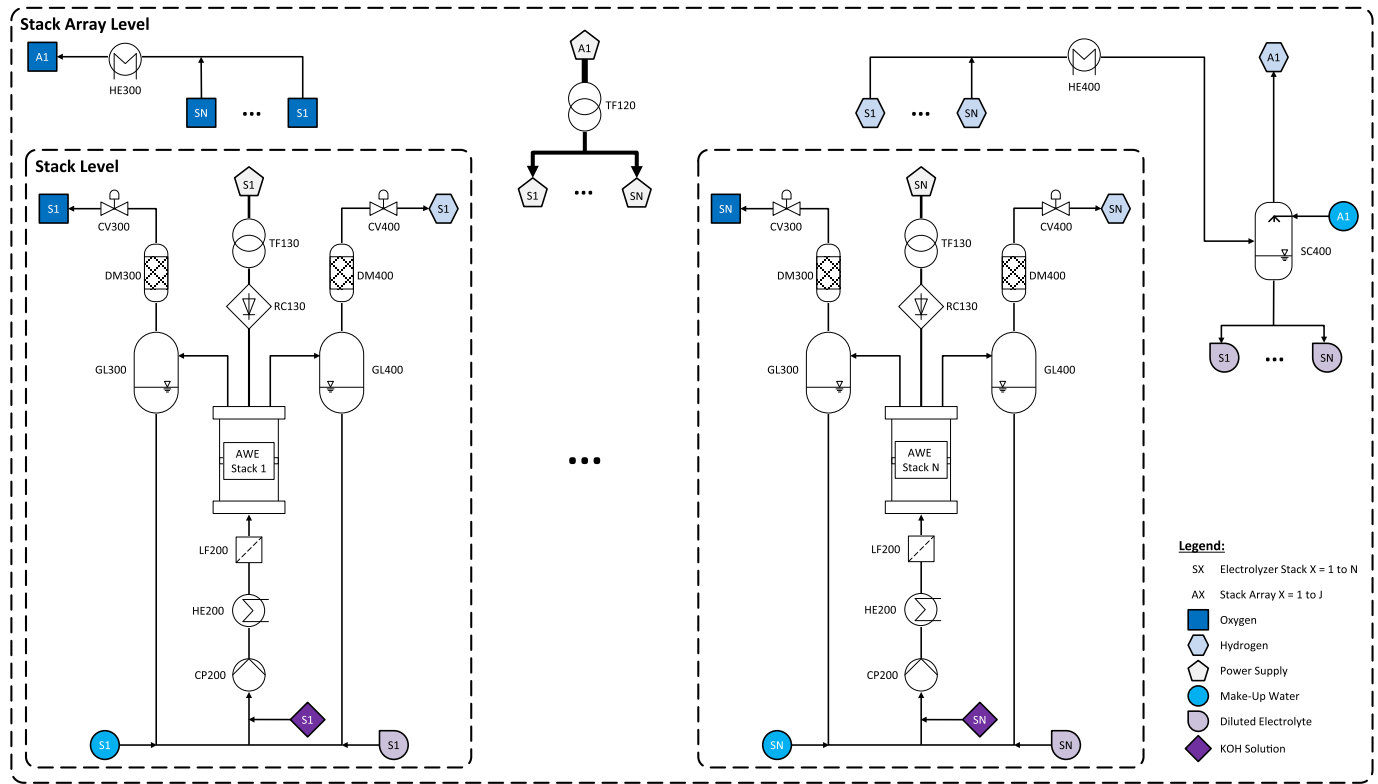


Fig. 8. Schematic representation of a typical stack array and stack-level BoP diagram for an AWE electrolyzer system, illustrating key components including the hydrogen and oxygen GMS at the stack array level, electrolyzer stacks, distribution voltage transformer, and scrubber. Schematic redrawn and summarized based on [89,90,100].

filtration is critical for preventing issues such as diaphragm clogging [105].

The lye flow rate is typically controlled based on the hydrogen production rate, with the set-point directly linked to the hydrogen output or the electrical current supplied to the system [89]. The lower limit of the flow rate is determined by the need for effective removal of gas bubbles from the electrode surface and sufficient heat transfer from the electrolyzer stack [106]. Conversely, the upper limit is defined by the maximum differential pressure values specified by the system suppliers to ensure equipment protection [107].

Industrial AWE systems typically have a minimum load threshold above 20 %, constrained by HTO safety limits. HTO levels between 4.0 % and 95.4 % pose a significant explosion risk, necessitating system shutdown and nitrogen purging when HTO exceeds 2.0 %, which represents 50 % of the LEL [108–110]. Under renewable energy scenarios, these constraints further reduce energy utilization efficiency from wind or solar power while increasing operational safety risks [111]. The HTO arises from three primary mechanisms: (i) cross-diaphragm diffusion due to hydrogen concentration differences; (ii) convection through the diaphragm caused by pressure differentials; and (iii) mixing of dissolved and liquid hydrogen in cathode and anode lye streams [112]. Key operational parameters affecting HTO include system pressure and lye flow rate. Reducing system pressure lowers hydrogen solubility but increases compressor energy demands and bubble coverage on electrode surfaces, leading to higher electrolysis energy consumption [112]. Conversely, at higher current densities, rapid bubble formation increases overpotential due to bubble resistance, further elevating energy demand [113].

According to Hu et al. [112], AWE systems can operate safely during high-load conditions without adjusting pressure or lye flow rates. However, under continuous low-load operation, the HTO approaches the safety boundary over time. At this point, two strategies are available: (i) maintaining constant operating conditions for high efficiency, risking

HTO reaching 2.0 % and causing shutdown, or (ii) reducing lye flow rate or system pressure to manage HTO and ensure continuous operation at lower efficiency. In the scenario of hydrogen production from renewable energy sources, operation (i) can result in frequent equipment shutdowns, which might not only negatively affect equipment lifespan but also waste all the renewable energy generated during the shutdown period. Additionally, nitrogen purging after shutdown is essential for safety, leading to significant hydrogen waste and energy losses during the system restart, making operation strategy (ii) beneficial in terms of energy utilization, equipment longevity, and overall safety.

Downstream of the stack, the mixture of lye and oxygen or hydrogen bubbles enters the respective gas-liquid separators (GL300 and GL400), where oxygen and hydrogen are separated from the lye solution. After separation, the lye solution is reintroduced into the lye circulation loop and fed back into the stack. The liquid level in the gas-liquid separators is typically maintained by pressure control and the injection of make-up water either directly to the lye circulation loop or to the oxygen gas-liquid separator, depending on the system design [89,100].

For **PEM systems**, the initial step of the WMS is identical to that of AWE systems (see Fig. 7), starting with the make-up water system as described above. However, since PEM electrolysis uses a proton exchange membrane as electrolyte instead of a KOH solution, a lye preparation system is not required, resulting in a less complex WMS. The absence of components such as lye tank, lye filter, and scrubber simplify both the system's design and operation, enabling it to focus primarily on delivering high-purity water directly to the electrolysis process.

During electrolysis, water is recirculated from the anode section of the stack, typically exiting at temperatures between 50 °C and 80 °C. At these elevated temperatures, DI water creates an aggressive environment, gradually leading to the release of metal ions such as iron (Fe^{2+} or Fe^{3+}) from wetted metallic components, including bipolar plates, diffusers, and stainless-steel piping. In addition to metal ions, other impurities can accumulate in the DI circulation loop as well. For example,

fluoride (F⁻), sulfates (SO₄²⁻), and organic fragments as a result of degradation due to the thermal and oxidative stress experienced by the Nafion membranes [114–116]. This ion release poses significant challenges for maintaining water purity during operation and protecting overall system integrity. It further accelerates long-term membrane degradation [117]. Consequently, an additional DI loop purification system is required to address these issues [52]. Within this purification system (see Fig. 9), IEX treatment is typically employed as the primary treatment process, utilizing strong acid cation (SAC) and strong base anion (SBA) exchange resins. The proposed system design for the application case described in this study is outlined in detail in **Chapter 6.2**. The design treatment capacity for the DI loop purification system is based on the maximum volume of water extracted from the DI circulation loop during peak hydrogen production. This calculation considers water losses resulting from hydrogen production, evaporation, and water dragged through the membrane via electro-osmosis, if this water is directed to the pure water tank rather than being fed directly back into the DI circulation loop [118]. To prevent impurity buildup, the treatment capacity of the DI loop purification system must be sized slightly larger than this maximum value with an additional buffer to account for impurities resulting from membrane degradation and corrosion [105]. Typically, depending on the design ratio of water circulation to water consumption (λ_{H_2O}), the treated water stream accounts for 1–10 % of the circulated stream [119]. In contrast, for AWE systems, this additional purification step is not necessary [105].

To minimize the thermal degradation mechanisms described above, the water in the loop is pumped by the DI circulation pump (CP200) through the DI loop heat exchanger (HE200) for temperature regulation and is then fed back into the electrolyzer stack. In addition to thermal membrane degradation, the degradation of SBA resin must also be considered when designing the DI loop purification system [120]. The purified water is then blended with the main flow in the oxygen gas-liquid separator (GL300) to maintain the required water quality and

reduce impurity levels.

As for AWE systems, the flow rate in the DI water circulation loop is typically controlled based on the hydrogen production rate. The lower limit of the flow rate is dictated by the need for effective heat transfer from the electrolyzer stack and the removal of gas bubbles from the electrode surface. The resulting flow regimes, as described by Maier et al. [121] in their review on mass transport in PEM water electrolysis, transition from single-phase flow (no oxygen production) to various forms of two-phase flow depending on oxygen production levels. At low current densities, the system operates in a single-phase water flow regime. As electrochemical activity and gas production increase, the flow progresses to a bubbly regime, where gas bubbles are dispersed within the liquid. With further gas production, bubbles coalesce into plugs or slugs, which fill the diameter of the channel. In churn flow, these slug bubbles deform, and smaller gas bubbles increasingly populate the liquid between them. As the flow transitions to the annular stage, water forms a thin film along the channel walls, while gas occupies most of the channel's cross-section. With even higher gas flow rates, the liquid film breaks into a dispersed gas-liquid mixture, known as annular-mist flow. Conversely, the upper limit of the flow rate is constrained by the maximum differential pressure values specified by system suppliers, ensuring the equipment's safety and structural integrity of the stacks [122–124].

If excessive water accumulates on the cathode side due to crossover through the proton exchange membrane, the automatic valve (PV400) activates, redirecting the excess water either back to the pure water tank (PWT100) or back into the DI circulation loop, depending on the system design. While doing so, the water is kept within the cycle, ensures proper system balance, and reduces the water footprint of the process.

4.4. Heat management subsystem

The HMS plays a pivotal role in both AWE and PEM electrolyzers by

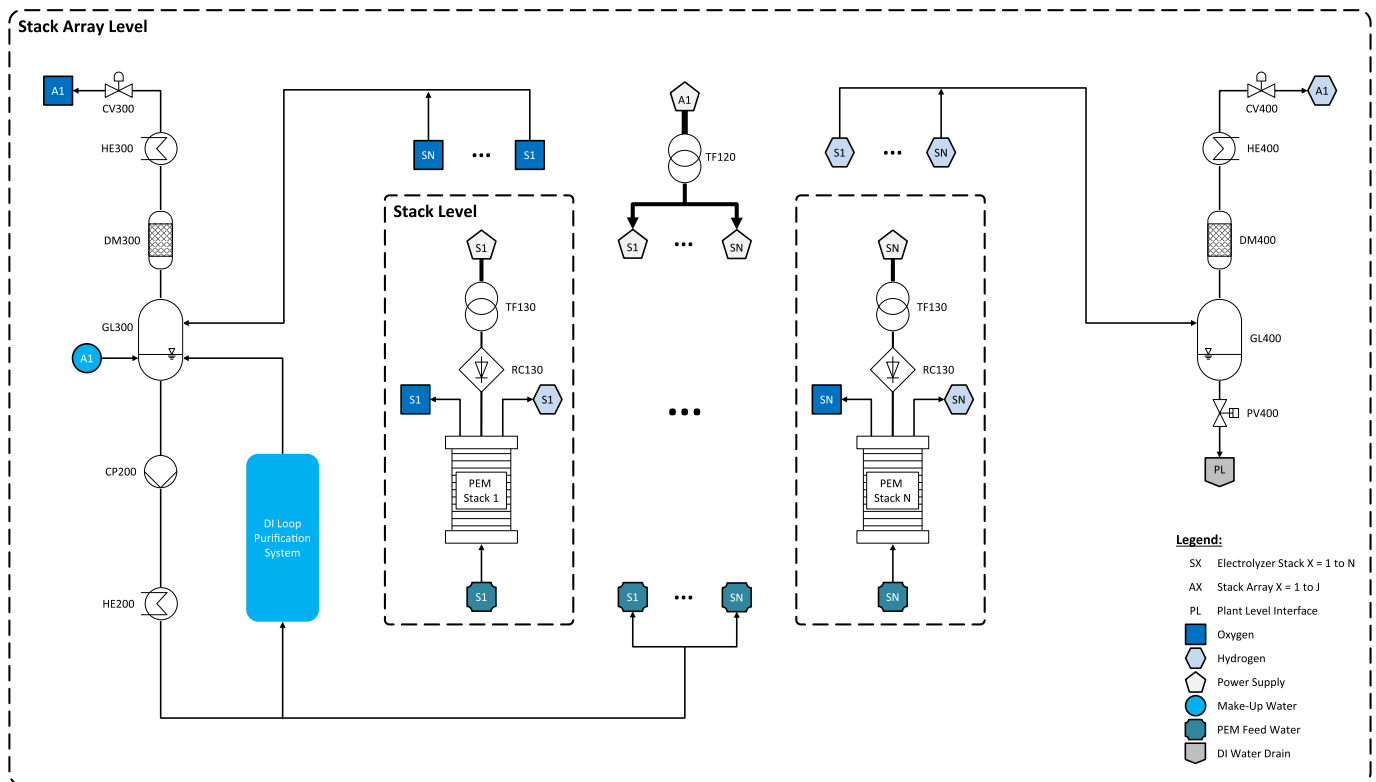


Fig. 9. Schematic representation of a typical stack array and stack-level BoP diagram for a PEM electrolyzer system, illustrating key components including the hydrogen and oxygen GMS at the stack array level, electrolyzer stacks, distribution voltage transformer, and DI loop purification System. Schematic redrawn and summarized based on [91,92,99,100].

ensuring optimal operating temperatures. For both systems, stack cooling primarily utilizes internal cooling via the lye heat exchanger (AWE) or the DI loop heat exchanger (PEM). The BOL heat exchanger design is compact and cost-effective but restricts performance as the electrolyzers degrade. To address this, it should be designed for EOL conditions, considering degradation to allow greater heat removal and enhance hydrogen production capacity [106]. Conventionally, the heat generated by the stacks (typically at 50 - 80 °C) is dissipated using dry coolers, although the choice of cooling technology ultimately depends on the specific site conditions [53,125].

Besides efficiency considerations for both technologies, accurate temperature control is particularly critical for PEM systems. The heat generated during operation must be efficiently removed to maintain the maximum cell temperature below the critical threshold of 80 to 90 °C, as determined by the thermal stability of the PFSA membrane [119]. Additionally, system suppliers typically recommend maintaining a temperature difference (ΔT) between the stack inlet and outlet of not more than 5 °C [54]. This helps minimize thermal gradients, preventing differential swelling of the Nafion membrane, mechanical stress, and degradation of the catalyst layer [119]. For AWE systems, higher values are reported; for example, DeNora recommends temperatures of up to 15 °C for their electrode packages [107].

To estimate the required flow rate for effective heat management, Ito et al. [118] and Villagra & Millet [119] introduced a simplified approximation using the dimensionless factor λ_{H_2O} . This factor represents the ratio of water pumped through the cell to the water consumed during electrolysis, providing a useful measure for optimizing cooling performance.

Assuming only liquid water is pumped through the anode compartment and all heat is extracted via the anodic water circuit, the required DI water flow rate to maintain a sufficient ΔT (in K) relative to the cell voltage U_{cell} (in V) can be approximated using Eq. (3):

$$\lambda_{H_2O} = \frac{2F}{M_{H_2O} \cdot C_{p,H_2O} \cdot \Delta T} (U_{cell} - U_{in}), \quad (3)$$

where F is the Faraday constant in C/mol, M_{H_2O} the molar weight of water in g/mol, C_{p,H_2O} is the heat capacity of liquid water at constant pressure in J/(g K), and U_{in} is the thermoneutral cell voltage at the operation conditions in V.

Plotting λ_{H_2O} over ΔT shows that small ΔT values require high water flow rates ($\lambda_{H_2O} \gg 1$), while larger ΔT values reduce water flow requirements. Heat extraction demands increase with operating voltage, and since U_{cell} typically rises over time, λ_{H_2O} should also be optimized for EOL conditions to ensure adequate cooling [119,126].

For low ΔT (< 5 °C), liquid water flow through the cell/stack ensures a liquid fraction above 95 % at atmospheric pressure. Conversely, at lower λ_{H_2O} values ($\Delta T > 5$ °C), water flow is reduced, lowering the liquid fraction. Given the low thermal conductivity of oxygen (25 × less than water), high gas fractions may impair heat removal. Pressurizing up to 5 bar can keep the gas fraction below 10 %, improving heat transfer. Ultimately, the water flow rate in a PEM system balances: (i) pumping energy, (ii) acceptable ΔT to minimize degradation, and (iii) effective heat removal to maintain cell durability. Increasing operating pressure further enhances heat extraction by reducing gas-induced thermal resistance [119,126].

Another approach for PEM temperature control decoupling flow rate from heat management could involve the use of an external cooling cycle. This would use dedicated cooling channels with a water/glycol coolant, similar to the systems applied in high-performance PEM fuel cells [127,128]. The key advantage of this approach is the enhancement of operational flexibility, combined with efficient temperature control, which is critical for the development of larger stack sizes.

When electrolyzers are installed close to sources of heat demand, the waste heat produced can also be utilized, resulting in higher overall system efficiency. Van der Roest et al. [125] investigated the feasibility

of using this waste heat either directly or for district heating. Their sensitivity analysis demonstrated that heat transport distance is a key factor in determining feasibility, with viable distances ranging between 1 and 3 km, depending on the use case. Approximately 14 - 15 % of the electricity input to the electrolyzer stack could be recovered as usable heat. For district heating, the electrolyzer waste heat could cover around 16 % of the total heat demand for the investigated neighborhood. A real-world example is the proposed 100 MW electrolysis system in Hamburg, Germany, which plans to utilize waste heat for district heating, with operations expected to begin in 2025.

5. Water quality requirements and impact of impurities

The quality of water used in electrolysis is a critical factor influencing system performance, efficiency, and durability. Impurities in the water can adversely affect electrolyzers in several ways. Cationic impurities such as Na^+ , Ca^{2+} , and Mg^{2+} can for example replace protons in the membranes of PEM electrolyzers, resulting in reduced ionic conductivity and diminished efficiency [129]. Anionic impurities, including halides such as chloride (Cl^-) and bromide (Br^-) or SO_4^{2-} , can induce severe corrosion in both AWE and PEM systems, especially at the anode under high-potential conditions, thereby damaging critical components [105]. Organic molecules, on the other hand, may form films on catalyst surfaces, obstructing active sites and decreasing reaction rates [105]. Impurities also contribute to broader systemic challenges in electrolysis systems. Catalyst poisoning, for instance, occurs when impurities such as metal ions adsorb onto the electrodes, preventing water molecules from accessing active sites, reducing reaction efficiency and slowing hydrogen production kinetics [129,130].

These challenges result in higher maintenance requirements, frequent component replacements, and increased costs, often necessitating additional water treatment processes to maintain system stability. The resulting specific make-up water quality requirements for AWE and PEM systems are typically defined by the electrolyzer system supplier but are often kept confidential due to the competitive and rapidly growing market. As a general guideline, most electrolysis systems recommend a maximum feed water conductivity of < 1 $\mu S/cm$, in accordance with the ASTM Type II standard [52], which corresponds to a TDS concentration of less than 0.5 mg/L. It is important to note that this serves only as a baseline, as system-specific water quality requirements may differ slightly. Notably, higher water quality does not negatively impact either AWE or PEM systems. Even if the threshold is slightly undershot, this is favorable to the process and poses no issue for the system design of the electrolyzers or the water treatment plant. Referring to the short calculation in Chapter 2.2, which puts the CAPEX of the water treatment plant and the electrolyzer system into perspective for large-scale electrolysis systems, opting for higher water quality seems to be a sensible approach.

To accelerate their market share growth in the rapidly expanding AWE technology business, De Nora and Thyssenkrupp Nucera have recently intensified their partnership and established a joint venture [131,132]. Thyssenkrupp Nucera, one of the leading system suppliers in this field, offers the largest currently available modular AWE system on the market, the Scalum module, with a capacity of 20 MW. While they have not disclosed specific water quality requirements due to confidentiality reasons, De Nora has provided this information indirectly for the zero-gap electrode package they supply to the process. Table 3 below presents the maximum allowable concentration of critical pollutants in the electrolyte loop, to ensure higher performance and extended lifespan of the electrode package [133].

These thresholds also indirectly determine the required feed water quality. A mass balance around the system can be used to identify the critical design parameter for the water treatment plant - specifically, the component that most rapidly approaches the specified thresholds within the expected electrode lifespan of > 5 years (performance drift of < 0.5 % per year). In this context, several factors must be considered,

Table 3

Maximum allowable concentration of some critical pollutants in the electrolyte loop according to electrode package manufacturer De Nora [133].

Component		Unit	Threshold
Iron	Fe ²⁺	mg/L	1
Chromium	Cd ²⁺	mg/L	5
Calcium/Magnesium	Ca ²⁺ /Mg ²⁺	mg/L	10
Chloride	Cl ⁻	mg/L	100
Carbonate	CO ₃ ²⁻	mg/L	10,000
Silica	SiO ₂	mg/L	20
Sulfate	SO ₄ ²⁻	mg/L	1000

including the KOH purity for the initial filling and preparation of the make-up solution, the corrosion rate of BoP materials, water and KOH losses during production, and the quality of DI water [133].

Industry experience indicates that the conductivity requirement for AWE systems can sometimes reach up to 5 $\mu\text{S}/\text{cm}$. However, as project scales increase, a clear trend has emerged among electrolyzer manufacturers toward significantly more stringent water quality standards, particularly for high-performance systems. In recent years, some manufacturers have even adopted water purity requirements exceeding the ASTM Type I standard. This shift aims to extend the operational lifespan of the KOH solution to at least five years before reaching the critical thresholds outlined in Table 3.

Alongside DI water quality, KOH purity plays a critical role in loop contamination. This is because industrial-grade KOH typically has a purity of only around 90 %, already containing many of the above listed impurities. These include components such as CO₃²⁻ in the form of K₂CO₃ ($\leq 0.61 \% \pm 0.26 \%$), Cl⁻ as KCl ($\leq 0.020 \% \pm 0.018 \%$), SO₄²⁻ as K₂SO₄ ($\leq 0.021 \% \pm 0.027 \%$), and Fe²⁺ ($\leq 0.0022 \% \pm 0.0023 \%$). Beyond that, contaminants such as Na⁺ as NaOH ($\leq 0.83 \% \pm 0.29 \%$), Ni ($\leq 0.0005 \% \pm 0.0001 \%$), Pb ($\leq 0.0028 \% \pm 0.0026 \%$), and insolubles in water ($\leq 0.05 \% \pm 0 \%$) can also be present [134–138].

Given the operating conditions and the fact that a 30 % KOH solution has a molarity of 6.85 M (equivalent to a calculated pH of 14.84), potential precipitation of components such as Ca(OH)₂ and Mg(OH)₂ must be taken into account, especially in the context of seawater composition. The solubility product constants of Ca(OH)₂ ($K_{\text{sp}}=5.5 \times 10^{-6}$ [113]) and Mg(OH)₂ ($K_{\text{sp}}=1.8 \times 10^{-11}$ [113,139]) in water at 25 °C indicate that both compounds are essentially insoluble under these conditions. This is further evidenced by their solubility limits, calculated as 8.7×10^{-2} mg/L for Ca(OH)₂ and 2.2×10^{-8} mg/L for Mg(OH)₂. Consequently, any excess Ca²⁺ or Mg²⁺ ions present as impurities will precipitate almost immediately, necessitating a removal strategy. This is achieved in practice by using a lye filter, which removes these impurities along with insoluble components that may already be present in the solution due to KOH impurities, as specified in the datasheets. A more detailed explanation is given in Chapter 5.1.1.

For PEM systems, DI water purity is even more critical than for AWE systems due to the use of sensitive Nafion membranes as the electrolyte. As a result, achieving higher purity levels is often mandatory to maximize stack lifetime, a crucial factor for commercial viability, with make-up water conductivity typically required to be as low as $\leq 0.1 \mu\text{S}/\text{cm}$ [52,130]. Many suppliers specify ISO 3696 Grade 2 or ASTM Type II DI water with a resistivity above 1 M Ω ·cm as the minimum requirement for commercial electrolyzer use, while Grade 1 or Type I DI water with a resistivity over 10 M Ω ·cm is preferred in order to achieve enhanced operation stability of the system [52,117]. When water quality for PEM systems is defined based on these standards, strict limits on specific impurities, such as Na⁺ as well as Cl⁻ levels below 5 $\mu\text{g}/\text{L}$ or a TOC concentration under 50 $\mu\text{g}/\text{L}$ apply. In this context, it is important to note that these water quality standards were originally designed for analytical laboratory use rather than for electrolysis. Consequently, the electrolyzer industry has adopted these standards, with supplier-specific modifications, to meet its unique operational needs.

Becker et al. [105] highlighted in their study the significant impact

that even trace amounts of impurities can have. They conclude that even when compliance with the ASTM Type II DI water standard is ensured, a 1 MW PEM stack operating continuously for a decade could be exposed to over 40 g of Na⁺ - an amount sufficient to ion-exchange nearly one third of the utilized membrane area. Moreover, because water is consumed stoichiometrically in the electrolyzer while its impurities are not, these contaminants may progressively accumulate in the cells and recirculation loop by several orders of magnitude. Collectively, these observations underscore the necessity of incorporating treatment with IEX resins into the recirculation loop and highlight the potential impact of even minimal impurity concentrations.

In line with these considerations, LANXESS recommends as part of the development of their new IEX product line especially for PEM systems, to set the make-up water quality below 1 $\mu\text{S}/\text{cm}$, combined with a DI loop purification system utilizing ultra-pure water (UPW) IEX resins to target a conductivity of the treated part stream of below 0.1 $\mu\text{S}/\text{cm}$ [140]. This approach has also been adopted as the basis for the conceptual development of an appropriate DI loop purification system design in this study.

5.1. Impact of impurities

In their widely cited work, Becker et al. [105] distinguished between exogenous impurities - contaminants introduced from external sources, such as water purification systems or reagents like KOH - and endogenous impurities, which originate within the electrolyzer system and BoP components. Furthermore, they proposed a classification scheme that categorizes four primary impurity types: cationic, anionic, organic, and inert. The same classification framework is also adopted in this study.

5.1.1. Impact on AWE systems

In AWEs, where OH⁻ serves as the primary charge carrier, cations do not directly compromise the membrane, ionomer, or electrolyte, unlike in PEM systems. Some **cationic impurities** frequently found in water and KOH electrolytes can even enhance the activity of certain OER catalysts.

Demnitz et al. [141] found in their recently published study that increasing the Fe-ion concentration in the electrolyte significantly enhances both HER and OER performance. With elevated Fe levels, they observed a reduction in HER and OER overpotential by 100 mV and 200 mV. The underlying mechanism involved the dynamic transformation of Fe species, where Fe dendrites formed during HER, while NiFeO(OH) species developed under OER conditions. Flow cell experiments further demonstrated a total overpotential reduction of 200 mV, resulting in a twentyfold increase in performance.

These findings align with previous research on cationic impurities in AWEs, where certain metal ions, such as Ni²⁺ and Fe²⁺, have been shown to enhance OER efficiency, whereas Zn²⁺, Cd²⁺, and Pb²⁺ act as catalytic poisons by increasing overpotential. The deposition of Fe onto Ni-based catalysts has been particularly well documented. Corrigan and Bendert reported that in purified KOH solution, OER overpotential at 8 mA/cm² increased after 10 charge/discharge cycles, whereas the addition of just 1 mg/L Fe led to a notable reduction in overpotential. Even trace amounts (0.01 %) of Fe deposition on the catalyst surface were sufficient to lower both OER overpotential and Tafel slope. Similarly, Fe, Ce, and Co, when co-precipitated on Ni(OH)₂ at concentrations above 10 %, further improved OER performance. In contrast, Zn²⁺, Cd²⁺, and Pb²⁺ increased overpotential at 16 mA/cm², thereby inhibiting catalytic activity [142–144].

The enhancement observed with Fe incorporation is attributed to two primary mechanisms: (i) an increase in electrical conductivity by up to a factor of 30 compared to pure Ni(OH)₂/NiOOH and (ii) modifications to the active catalytic sites, where γ -NiOOH has been identified as the most active OER phase in the absence of Fe [145].

Other cationic species, such as Ca²⁺ and Mg²⁺, introduce additional challenges. As discussed in the previous chapter, even trace amounts of these ions can precipitate under alkaline conditions, typically forming

insoluble hydroxides or carbonates. These deposits tend to accumulate directly on the catalyst surface, blocking active sites and thereby reducing the number of electrochemically accessible reaction centers. In parallel, scaling layers or insoluble particles can clog separator pores, further restricting mass transport. Together, these effects lower the effective catalytic activity and hinder reactant supply, leading to diminished system efficiency [146].

Anionic impurities can also adversely affect AWE systems, primarily by substituting charge carriers in the electrolyte and contributing to corrosion issues within the BoP. Among these, CO₂ is a particularly concerning impurity in alkaline environments, as it readily reacts with the KOH solution. At an ambient concentration of approximately 400 ppm, CO₂ undergoes a reaction that leads to the formation of HCO₃⁻ and CO₃²⁻ anions, as described by the following Eq. (4) and 5 [147]:



This leads to a decrease in electrolyte conductivity, thereby impairing overall cell performance. Kiss et al. [148] and Varcoe et al. [147] attributed this effect to the larger size of these species, which consequently results in reduced ionic mobility. The hydrated radii of HCO₃⁻ and CO₃²⁻ are 3.64 Å and 3.94 Å, both exceeding the 3 Å radius of OH⁻. As a result, their ionic mobilities are significantly lower, with relative values of 0.22 for HCO₃⁻ and 0.36 for CO₃²⁻ in comparison to OH⁻.

Similarly, halide ions like Cl⁻, introduced through impure feed water, can initiate corrosive side reactions that damage electrodes and other components [105].

The impact of **organic contaminants** on AWEs remains insufficiently investigated. These impurities, often introduced through low-quality make-up water, pose potential risks to system performance. In commercial AWEs utilizing nickel-based catalysts, although the anode potential is generally high enough to initiate oxidation, catalyst passivation may hinder the complete breakdown of organic compounds [105]. Under typical AWE operating conditions, the anode potential should facilitate the oxidation of organic contaminants into carbon monoxide (CO) and CO₂. As previously discussed, CO₂ presents significant challenges in alkaline electrolytes. Similar to PEM electrolyzers, both CO₂ and CO may also contribute to product hydrogen contamination [105]. Additionally, specific organic compounds could impose a chelating effect on nickel catalysts. For example, ethylenediaminetetraacetic acid (EDTA) [149] and [S,S]-ethylenediamine disuccinic acid (EDDS) [150], both widely used in metal recovery, have demonstrated the ability to form stable metal complexes. This chelation effect could lead to or accelerate catalyst degradation. Consequently, careful consideration must be given when water containing unknown organic contaminants is used as a feed source [105]. In general, classifying the different TOC species present in the feed water is advisable during project planning to facilitate the selection of appropriate removal processes.

Inert impurities can become an issue in AWE systems as well, as outlined already in Chapter 5. The highly alkaline pH can thereby lead to the precipitation of metal ions due to the limited solubility of their oxides and carbonates. The primary concern associated with precipitation is the clogging of porous components, such as the separator or electrodes, which can hinder mass transport. However, this issue is likely to arise only in cases where high concentrations of carbonate or low-solubility metal ions are introduced, such as in the event of a failure in the water purification system [105].

Despite advancements in understanding the impact of impurities on AWEs, significant knowledge gaps persist, particularly regarding their effects at both the single-cell and stack level. Key research priorities include investigating the behavior of organic contaminants and improving the selectivity of OER catalysts in the presence of Cl⁻ ions. This is particularly relevant for direct seawater electrolysis and the utilization of lower-quality water sources to reduce purification costs

[105]. While AWEs exhibit resilience to low impurity concentrations, the long-term implications for the durability and efficiency of modern high-performance systems remain uncertain. Addressing these challenges is essential for the development of more robust, cost-effective, and sustainable electrolysis technologies [105].

5.1.2. Impact on PEM systems

Poor water quality is one of the primary causes of stack failure in PEM systems [129,151], although these electrolyzers can achieve reported lifetimes exceeding 60,000 operating hours. Factors influencing their lifespan are not limited to water quality alone but also include operating conditions, voltage fluctuations, gas leaks, and anode dissolution. Nevertheless, many electrolyzer components, such as membranes, ionomers in the catalyst layer, catalysts, and porous transport layers, are quickly affected by impurities [129].

Cationic impurities, primarily derived from feed water (e.g., Na⁺, Ca²⁺, and Mg²⁺) or corrosion products (e.g., Fe²⁺ and Fe³⁺) from wetted metallic components in the BoP, are particularly problematic for PEM systems. They adversely affect PEM performance mainly by reducing membrane conductivity [152,153]. PFSA-based membranes, such as Nafion, exhibit exceptionally high conductivity in aqueous environments owing to the hyperacidity of their SO₃ terminal groups, which promotes the generation of mobile H⁺ ions [154]. However, most cations demonstrate a higher affinity for the SO₃ groups than protons, resulting in proton displacement and a subsequent decline in proton conductivity [152,153]. Typically, PFSA membranes in liquid water display ionic conductivities in the range of 0.05 - 0.2 S/cm [154], but this value may decrease by one to two orders of magnitude when complete proton exchange with metal cations occurs [155]. However, the impact of cationic impurities on membrane properties is not uniform; for example, higher valence ions are preferentially absorbed, leading to their accumulation within the membrane even at very low aqueous mole fractions [105]. For instance, Fe³⁺ exhibits an equilibrium constant approximately 5000 times greater than that of Na⁺ [156]. Kelly et al. [156] investigated the effect of impurity cations on the conductivity of Nafion 117 measured at a depth of 50 μm and identified a threshold concentration beyond which a distinct step change in conductivity occurs. Specifically, ions such as Na⁺, Cu²⁺, Ni²⁺, and Fe³⁺ were observed to significantly reduce conductivity only when their concentrations exceeded 10 mg/L in water.

In addition to diminishing conductivity, cationic impurities can also impair the membrane's water transport characteristics and overall stability. Adsorption of cations such as Na⁺ and Ca²⁺ has been shown to disrupt the water balance by increasing the water transfer coefficient while reducing the membrane's water content [157]. Okada et al. [158] demonstrated that, for Nafion 115, the water transfer coefficient increased from 2.5 to over 10 when all the protons in the membrane were replaced with Ca²⁺.

Bas et al. [159] observed that thermal stability of PFSA membranes is also influenced by the presence of cations. In their study, the onset temperature for thermal degradation of the SO₃ group increased when the Nafion 211 membrane was contaminated with Ni²⁺, with this effect becoming evident at a Ni²⁺/H⁺ ratio of 0.2. Moreover, they concluded that the performance of PFSA membranes depends less on the cation concentration in the feed solution - as typically reported in the literature - and more on the cumulative number of cations that have interacted with the membrane. Consequently, even very low concentrations of cationic contaminants, when accumulated over extended periods, may lead to significant degradation of membrane performance.

The catalyst layers in PEM electrolyzers typically incorporate an ionomer, which serves as an ion-conducting phase, in order to enhance the electrochemically active surface area. This surface area corresponds to the region where water as the reactant, protons, and the catalyst surface are in direct contact [160]. The ionomer used in PEM is generally composed of PFSA, which, upon exposure to cations, experiences similar challenges as the membrane itself [160]. While proton depletion

within the ionomer can contribute to an increase in cell resistance, the catalyst layers are relatively thin, generally measuring less than 50 μm [161], with ionomer coatings on the catalyst surface being several orders of magnitude thinner. As a result, the predominant concern is the effective loss of electrochemically active surface area due to the deactivation of proton transport, rather than the increase in resistance [105].

An additional mechanism through which metallic cations degrade PEM water electrolyzer performance is their deposition on the cathode, where potentials typically range from -100 to 0 mV relative to the reversible hydrogen electrode (RHE) [162]. Metal cations with a standard reduction potential above 0 V relative to this reference potential can undergo reduction, resulting in metal accumulation on the cathode catalyst surface and a subsequent decline in electrochemically active surface area. This effect can be further intensified by underpotential deposition, particularly in the presence of Cl^- ions [163].

A notable consequence of Fe^{2+} contamination is the initiation of the Fenton reaction, which facilitates the decomposition of peroxide into highly reactive hydroxyl radicals [130]. These radicals are known to attack the polymeric backbone of PFSA, significantly contributing to membrane thinning in PEM fuel cells and related systems [57,164–166]. In contrast to PEM fuel cells, where membrane degradation takes place on both, the anode and cathode sides, various studies on PEM systems have shown that thinning is primarily taking place on the cathode side [167,168]. At typical cathode potentials (< 0 V vs. RHE), crossover oxygen is primarily reduced via a two-electron pathway to form hydrogen peroxide [169]. Membrane thinning has been reported to be more pronounced at low current densities, where oxygen crossover is more substantial, and at elevated temperatures around 90 °C. Additionally, accelerated cell degradation has been observed even at low Fe^{3+} concentrations between 1 and 10 ppm [170,171]. While most studies have focused on Fe^{2+} as a catalyst for peroxide decomposition, other transition metal cations may also contribute to the generation of hydroxyl radicals and associated membrane degradation [172].

In contrast to cations, which can substitute protons within the membrane and ionomer, **anionic impurities** interact through alternative mechanisms. A prominent concern is the initiation of parasitic side-reactions such as the CER, which can degrade hydrogen purity and accelerate metallic corrosion as well as membrane degradation [130]. It is of particular concern due to its common presence in seawater at high concentrations and its strong impact on PEM electrolyzer performance. Chloride contamination represents a critical degradation pathway, as Cl^- ions at the anode undergo competitive oxidation to chlorine gas (Cl_2 , $E^\circ = 1.36$ V vs. SHE) and hypochlorous acid (HOCl , $E^\circ = 1.48$ V vs. SHE), both of which occur within the typical operating potential window and are thermodynamically competitive with the OER ($E^\circ = 1.23$ V vs. SHE) [173]. HOCl , which predominates in acidic environments, is a highly reactive oxidant capable of attacking PFSA membranes and accelerating catalyst dissolution, with its strong oxidative reactivity in such media [174]. Experimental studies confirm these effects: under chloride exposure in trace amounts, Kuhnert et al. [175] reported a 23 % increase in cell voltage after just 50 h, alongside catalyst detachment and a fourfold increase in fluoride emission rate, a clear marker of membrane degradation. Consequently, system-level reviews emphasize that even trace chloride levels compromise durability and efficiency, highlighting the necessity of rigorous feed-water purification strategies to mitigate chlorine-related side reactions [105]. Similar mechanisms may extend to other halide anions such as F^- , Br^- , and I^- , though chloride remains the most critical due to its prevalence.

Most anionic impurities are of exogenous origin, with the exception of F^- and SO_4^{2-} , which are generated as byproducts of membrane degradation [105]. In addition to promoting undesired side reactions, halide ions are particularly prone to adsorption onto the catalyst surface, given that the platinum cathode of a PEM typically operates at a negative potential ranging from -0.1 to 0 V vs. RHE [176]. The adsorption strength follows the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$ [177], with I^- and Br^- exhibiting the potential for irreversible adsorption at sufficiently high

concentrations. Nevertheless, as HER on platinum in acidic media remains a rapid reaction, minor anion contamination is unlikely to result in significant performance degradation [105].

SO_4^{2-} and bisulfate (HSO_4^-) anions arise as additional ionic species from membrane degradation. SO_4^{2-} anions are well known for their specific, potential-dependent adsorption onto platinum catalyst surfaces. Their adsorption intensity peaks within a potential range of 0.2 to 0.8 V vs. an Ag/AgCl reference electrode, with nearly complete desorption occurring at -0.2 V vs. Ag/AgCl [178].

At typical PEM cathode potentials (< 0 V vs. RHE) and under the locally acidic pH conditions imposed by the Nafion ionomer, H^+ adsorption dominates, effectively inhibiting SO_4^{2-} adsorption [179]. In contrast, at the anode, elevated SO_4^{2-} concentrations (0.05 M H_2SO_4) have been shown to adsorb onto the iridium catalyst surface, shifting the onset of the OER to higher potentials [180,181]. However, as the SO_4^{2-} concentration generated from internal membrane degradation is expected to remain in the ppb range, its impact is likely negligible [105].

Organic impurities encompass a broad spectrum of species and remain relatively uninvestigated. In PEM systems, organic contaminants may impair electrolyzer performance through two primary mechanisms: (i) catalyst poisoning via adsorption on the surface, reducing electrochemical activity, and (ii) acceleration of catalyst dissolution [182]. Unpolar, short-chained organic molecules such as urea, halogenated disinfection by-products, or trihalomethanes are particularly difficult to remove during water treatment [183]. These fractions, however, are generally underrepresented in seawater feedstocks and are of greater relevance for freshwater sources such as river water or recycled wastewater effluents [184,185]. For intakes located near municipal wastewater treatment plant outfalls or river mouths, this may constitute a site-specific concern, necessitating an adapted treatment concept that incorporates a TOC-UV step and a mixed-bed ion-exchange polisher, resulting in an expected rejection of such components of more than 90 % [183,184].

Non-ionic species are expected to have minimal impact on membranes and ionomers, particularly in PFSA, which have been extensively studied in analogous applications such as direct methanol fuel cells [105]. Beyond direct catalyst poisoning, the oxidation of organic molecules to CO and CO_2 introduces additional impurities into the system. While this is unlikely to cause significant issues at the anode, crossover to the cathode could be detrimental, as adsorbed CO block active sites on the platinum catalyst [186]. Furthermore, hydrogen purity may be decreased. However, additional research, particularly on the long-term effects of low-concentration exposure, is necessary to reliably assess the impact of organic contaminants.

The final category of contaminants includes **inert impurities**, such as solid particles, which can induce mass transport limitations. These particles may originate from external sources or arise due to deficiencies in the water purification system, leading to their accumulation and subsequent obstruction of membrane pores, ultimately hindering ion transport [105].

In summary, several critical challenges arise in assessing the impact of impurities on PEM electrolyzers. A primary concern is the need to better understand the effects of low-concentration impurities on electrolyzer longevity under realistic operating conditions. While many studies investigate high impurity concentrations to accelerate degradation processes, practical systems typically operate over prolonged durations (> 10,000 hours) under low impurity exposure. Gaining insight into these long-term effects remains essential for ensuring the durability and reliability of electrolyzers in real-world applications [130].

5.2. Accelerated stress test protocols

Without long-term data under realistic operating conditions, fully understanding the effects of impurities and the associated degradation mechanisms remains difficult. Moreover, comparing results across the literature is hindered by variations in operating conditions and testing

protocols. To address this, the development of standardized accelerated stress testing (AST) protocols is crucial for inducing specific degradation pathways and assessing the durability of new materials within a practical timeframe [130]. However, the current state-of-the-art lacks a clear and consistent definition of accelerated testing. In many cases, so-called accelerated tests merely involve variations from nominal operating conditions that increase degradation, rather than systematically targeting specific mechanisms [187].

At present, only a limited number of studies address this topic. Tomić et al. [187], Kuhnert et al. [188], and Urbano et al. [123] propose AST protocols related to PEM systems, while Malkow and Pilenga [124] present harmonized protocols for assessing performance degradation in low-temperature water electrolyzer stacks, including AWE, PEM, and AEMWE. These protocols enable systematic evaluation and comparison of degradation behavior across different systems. However, their primary focus lies on operational stressors such as current density, dynamic electrical operation, AC ripple, stack temperature, pressure, and lye or water inlet flow rate, with only limited attention given to water impurities. Water contaminants remain underrepresented and are typically limited to a narrow selection of ion species. Further research is required to comprehensively assess the influence of water impurities and to adapt existing AST protocols accordingly. An AST protocol targeting water impurities could involve operating the electrolyzer under defined conditions while systematically introducing specific contaminants, either individually or in defined mixtures, at controlled concentrations to evaluate their effects on performance and material degradation.

6. Water treatment systems for AWE and PEM

UPW is frequently cited as the process water quality grade for green hydrogen production. However, its definition is highly context-dependent and varies considerably across application cases. Most published water treatment concepts for UPW production from seawater feedstocks originate from the semiconductor industry [189–192], where purity requirements are far more stringent than those relevant for hydrogen electrolysis. Semiconductor-grade UPW, as defined by standards such as SEMI F63, demands, for example, resistivity ≥ 18.2 M Ω -cm, TOC < 1 μ g/L, ionic contaminants at sub-ppb levels, and virtually no particulate or microbial content. Meeting these specifications requires a multistage treatment process involving advanced pre-treatment, double-pass reverse osmosis, multiple stages of UV oxidation, membrane degasification, continuous electrodeionization or mixed-bed ion exchange, and final submicron filtration, as outlined in SEMI F61.

By contrast, descriptions of systems designed specifically for hydrogen applications remain limited. In particular, there is a lack of suitable literature addressing systems capable of meeting the specifications relevant for hydrogen production from seawater. To address this gap, a make-up water and DI loop purification system were developed for a reference project site in Eastern Australia as part of this study. These systems were designed to achieve the targeted DI water quality outlined in **Chapter 5** and to provide a reference plant design that can serve as a technical foundation for the ongoing discourse. The seawater quality data used for this purpose, sourced from [193], are summarized in **Table 4**.

Consequently, semiconductor-grade UPW systems offer significant potential for simplification when adapted to produce ASTM Type I/II-grade water, which is sufficient for hydrogen electrolysis. Such simplification can reduce CAPEX, OPEX, and overall system complexity by avoiding process-related overdesign.

6.1. Make-up water system

Two systems were developed: MWS1, featuring pressurized dual media filtration (DMF), a full second-pass (FSP) RO system, and continuous electrodeionization to meet ASTM Type II DI water requirements; and MWS2, which includes an additional IEX mixed bed

Table 4

Seawater composition at project site in Eastern Australia adapted from [193].

Parameter		Unit	Minimum	Average	Maximum
Temperature	T	°C	15.0	20.0	25
pH		-	7.5	8.1	8.7
Calcium	Ca ²⁺	mg/L	406.0	458.0	510.0
Magnesium	Mg ²⁺	mg/L	1100.0	1300.0	1500.0
Sodium	Na ⁺	mg/L	10,142.0	11,071.0	12,000.0
Potassium	K ⁺	mg/L	350.0	475.0	600.0
Barium	Ba ⁺	mg/L	0.0	0.0	0.0
Strontium	Sr ⁺	mg/L	6.6	8.2	9.7
Carbonate	CO ₃ ²⁻	mg/L	0.4	9.7	19.0
Bicarbonate	HCO ₃	mg/L	106.0	119.0	132.0
Sulfate	SO ₄ ²⁻	mg/L	2300.0	2942.0	3584.0
Chloride	Cl ⁻	mg/L	18,051.0	19,793.5	21,536.0
Bromide	Br ⁻	mg/L	65.0	70.5	76.0
Fluoride	F ⁻	mg/L	0.7	1.1	1.4
Nitrate	NO ₃	mg/L	0.0	0.1	0.2
Boron	B	mg/L	3.4	4.6	5.8
Silica	SiO ₂	mg/L	0.1	0.2	0.3
TDS	TDS	mg/L	32,531.3	36,252.8	39,974.4

polisher downstream of the continuous electrodeionization for cases requiring ASTM Type I DI water (see **Fig. 10**). The water treatment plant has a peak production capacity of 4800 m³/d while providing full system redundancy. This value corresponds to the DI water demand during peak hydrogen production of a 1 GW electrolyzer system with an efficiency of 75 %. It was calculated based on a specific water consumption of 10.5 kg H₂O per kg H₂ produced, which includes the stoichiometric requirement plus a contingency of 1.5 kg H₂O per kg H₂.

The system starts at the seawater interface, which includes three seawater feed pumps (IP200) to transport seawater into the plant, a sampling line for continuous monitoring of key water quality parameters such as conductivity, pH, temperature, TOC, and redox potential, and a dosing station for sodium hypochlorite (NaOCl) to mitigate biofouling of downstream equipment [194,195]. The seawater intake system, backwash water basin (BT900), outfall basin (OFT900), and building structures are not further discussed in this study, as they are highly site-specific and represent common infrastructure requirements across all desalination technologies. Brine management is achieved through outfall pipes equipped with diffusers, as applied in the vast majority of large-scale SWRO projects [196]. The low environmental impact of this approach has, among other evidence, been confirmed by long-term before-after monitoring at the Sydney Desalination Plant with a production of 250,000 m³/d, which detected no persistent ecological effects from brine discharged through high-pressure diffusers. Reef fish communities showed even temporary increases in abundance and diversity during operation but returned to background levels after discharge ended, indicating no lasting effects. Benthic invertebrates exhibited only minor, localized shifts within 100 m of the outfall, driven by hydrodynamic changes rather than salinity, which remained within 1 psu of ambient [197,198]. Outfall design is routinely supported by advanced recirculation and mixing simulation studies, a standard engineering practice and regulatory requirement during environmental assessments [196,199]. These findings demonstrate that well-designed diffuser systems at large-scale facilities effectively mitigate environmental risks, thereby making adverse impacts from smaller plants with lower discharge volumes even more unlikely.

Following this, the pre-treatment section features multiple dosing stations for sulfuric acid (H₂SO₄) for pH adjustment to a target value of 7.5, ferric chloride (FeCl₃) as coagulation agent, and polymer to enhance flocculation [200]. This stage also includes four horizontal pressurized dual media filters (DMF300) designed to remove suspended particles. Each filter consists of three layers: a gravel support layer, a filter sand layer, and a hydroanthracite layer, with a surface filtration area of 15 m² per filter. The filtration velocity is conservatively set at 10.1 m/h during normal operation, increasing to 13.4 m/h when one filter is in backwash. Backwashing is performed using two sets of blowers (BB300) and

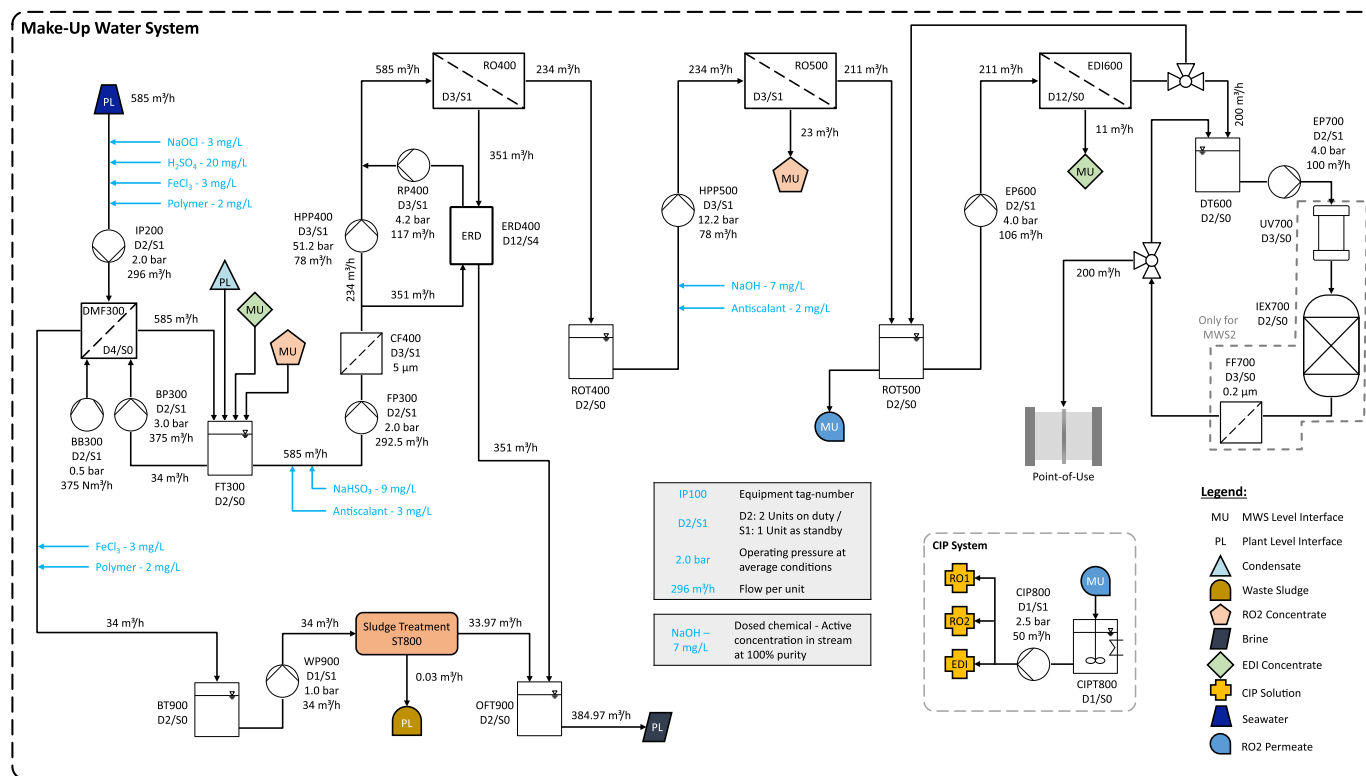


Fig. 10. Schematic of the MWS1 and MWS2 water treatment systems. MWS1 includes pressurized DMF (DMF300), an FSP RO system (RO400 & RO500), and CEDI (EDI600) to produce DI water in compliance with ASTM Type II standards. MWS2 features an additional IEX mixed-bed polisher (IEX700) to achieve ASTM Type I DI water. If even more stringent TOC thresholds are targeted, a TOC-UV (UV700) can be included. The figure also provides details on equipment sizing, pressure levels, and active chemical concentrations.

pumps (BP300), operating at air and water velocities of up to 50 m/h to ensure effective filter regeneration at least once per day [194]. The treated seawater is then collected in the filtered water tank (FT300) before being pumped downstream to the RO system by the filtered water pumps. Intermediate tanks in the design are sized to provide sufficient volume for a 10 min retention time, ensuring stable operation.

The RO system represents the heart of the plant. The first RO stage (RO400) incorporates shared dosing stations for antiscalant and sodium bisulfite (NaHSO₃) to control scaling and to perform dechlorination, respectively [200]. It further includes four RO trains, each equipped with a 5 μm cartridge filter for membrane protection purposes, high-pressure pumps (HPP400) to drive the RO process at a design recovery of 40 %, and RO racks consisting of 24 pressure vessels (PV), each housing six SWRO membrane elements (e.g., high rejection module TM820V-440 from Toray [201]). The average flux for the RO1 membranes was set at 13.6 l/(m²h), with an assumed average membrane age of 3.5 years and a salt passage increase of 7 % per year. Additionally, the design considers as isobaric energy recovery devices e.g., PX-180 units from ERI (ERD400) with a dedicated recirculation pump (RP400) for each train. This setup reduces the flow through the HPPs by effectively recovering around 95 % of the residual pressure from the brine stream, achieving a size reduction of 60 % at the given RO1 design recovery. The permeate is then subsequently directed to the RO1 permeate tank (ROT400).

From there, the RO1 permeate is pumped to the second RO stage (RO500) for further treatment. RO2 features shared dosing stations for antiscalant and sodium hydroxide (NaOH) for pH adjustment to a target value of 9.5, which enhances boron and CO₂ removal. The stage includes four RO trains, each equipped with a second set of HPPs (HPP500) and ten PVs arranged in a concentrate-staged configuration. This setup consists of six PVs on the first level, three PVs on the second level, and one PV on the third level, a design essential for achieving the targeted

high RO2 recovery rate of 90 %. All RO2 PVs are equipped with six BWRO membrane elements (e.g., high rejection module TM720D-440 from Toray [202]). The average flux for the RO2 membranes was set at 29.4 l/(m²h), with an assumed average membrane age of five years and a salt passage increase of 5 % per year. The concentrate stream, with a TDS concentration of up to 3200 mg/L, is recovered and returned to the filtered water tank to dilute the incoming seawater stream, increasing the overall plant recovery. The RO2 permeate is then directed to the RO2 permeate tank (ROT500).

For final water polishing in MWS1, the system incorporates a CEDI stage consisting of three CEDI feed pumps and 12 CEDI stacks (EDI600, e.g., high-flow module IP-VNX-MAX-1P from Ionpure [203]), designed to produce DI water with a quality exceeding 1 MΩ·cm while operating at a recovery rate of up to 95 %. The rejected concentrate stream is directed back to the filtered water tank for efficient resource management. For projects of this scale, on-site EDI diluate storage tanks with a capacity equivalent to 6–48 hours of peak demand is typically applied to ensure operational stability and to account for potential system interruptions. To mitigate CO₂ contamination of the water during storage, the tanks are equipped with either a CO₂ filter or a nitrogen blanket. Depending on the required process water specification, water is either supplied directly from the storage tank to the electrolyzer system when ASTM Type II quality is sufficient (configuration MWS1), or it undergoes additional treatment in a downstream point-of-use polishing unit to meet ASTM Type I requirements (configuration MWS2). The polishing unit counteracts potential contamination introduced during storage and ensures continued compliance with the targeted process water quality, which is particularly critical at elevated purity levels.

For MWS2, an additional IEX mixed-bed polisher stage (IEX700), filled with one-time-use UPW resin from DuPont in H⁺/OH⁻ form (e.g., AmberTec™ UP6040 H/OH [204]), is installed downstream of the CEDI. The system design includes two vessels in lead-lag configuration, each

equipped with a dedicated set of valves to switch between mixed bed positions and to isolate vessels as needed. This setup provides full system redundancy, ensuring continuous operation even during resin replacement. When required by project specifications, a fine filter (FF700) with a pore size of 0.2 μm can be added downstream of the mixed bed. For TOC thresholds exceeding 50 $\mu\text{g/L}$, as defined by the ASTM Type I standard, a TOC-UV (UV700) can be incorporated upstream of the mixed-bed polisher as an additional process unit in the system design. TOC-UV system operating at a wavelength of 185 nm is employed to degrade TOC to CO_2 at a rate of approximately 70 %, depending on the TOC species [205,206]. CO_2 is subsequently removed by the SBA resin in the IEX polisher mixed bed.

The treated water is then sent to the DI water interface, which includes a sampling line for continuous quality monitoring (conductivity, pH, temperature, TOC, and SiO_2), a recirculation line with a three-way control valve returning to the EDI diluate tank (DT600) to prevent stagnation, and a nitrogen-blanketed pure water tank (PWT100) for storage prior to injection into the electrolyzer system via distribution pumps (PWT100 and CP100 are shown in Fig. 6 and Fig. 7). Depending on process water management within the electrolyzer plant, direct injection into scrubbers or gas/liquid separators through the EDI diluate pumps (EP700) is also a viable solution.

As the electrolyzer capacity factor can fluctuate significantly due to renewable energy intermittency, process water demand also varies throughout operation. To accommodate for hourly demand fluctuations, the plant is designed for flexible operation in the range of 20–100 %. In addition, both the EDI diluate line and the polisher unit line are equipped with three-way valves and corresponding recirculation lines back to the upstream tanks. This configuration allows the units to remain in operation even when demand does not match the instantaneous water production. By preventing rapid shutdowns in response to sudden demand fluctuations, the design helps protect water quality and extend unit lifetime in the WTP. It also reduces flushing water losses by avoiding frequent on/off cycling of one or more units in response to minor load changes.

Auxiliary systems provide essential support to the desalination process, including a cleaning-in-place (CIP800) station designed for periodic membrane cleaning, backwash water transfer pumps (WP900), and a sludge treatment unit (ST900) that effectively manages solid waste generated during filter backwash in the pre-treatment process.

The centrifugal pumps considered for MWS1 and MWS2 were in accordance with the ISO 5199 standard. Material selection played a crucial role, as it directly influenced both system performance and cost. The materials chosen for the plant design were optimized for durability, corrosion resistance, and cost-efficiency in the desalination environment. Tanks are constructed from polyethylene (PE) and the horizontal DMFs are fabricated from rubber-lined carbon steel. For the seawater interface to RO1, high-pressure (HP) equipment ($> \text{PN}10$), such as pumps, valves, fittings, and piping, utilizes super duplex stainless steel with a pitting resistance equivalent number (PREN) greater than 40 (e.g., 1.4410), offering superior corrosion resistance in highly saline environments. Low-pressure (LP) components ($\leq \text{PN}10$) are made of PE for cost and weight reduction. Downstream of RO1, duplex stainless steel with a PREN > 30 (e.g., 1.4462) is employed for HP equipment, while LP components are again in PE. Beyond RO2, materials transition to stainless steel with a PREN > 20 (e.g., 1.4404) for HP equipment, while LP components switch to polypropylene (PP). These material choices ensure longevity and reliability while optimizing the CAPEX of the system. It is further backed by the state-of-the-art material selection in SWRO desalination [207].

The system performance was projected using supplier design software for the different process stages. For the RO membranes Toray DS2 (version 2.3.3.211(1.2.8.124)) was used. CEDI projections were made with IP-PRO (version 5.1), with a safety factor of 1.3 applied to the obtained TDS concentration of the RO2 permeate [208]. The IEX mixed bed polisher in MWS2 was simulated using DuPont's Wave Software,

version 1.83.

Due to the varying operation conditions, different design cases (see Table 5) had to be prepared in order to define the operational envelope of the SWRO system, ensuring the design can accommodate fluctuations in feedwater properties and membrane aging while maintaining performance. Increased water temperature enhances diffusion through the membrane, leading to higher permeate TDS and lower feed pressure requirements. Higher feed TDS increases osmotic pressure, necessitating higher feed pressure. Over time, membrane aging reduces water permeability and increases salt passage, resulting in elevated permeate TDS and greater feed pressure [208].

Case 1 represents typical operation, with average feed conditions and membrane age, serving as the baseline. Case 2 models the most challenging conditions - high feed TDS, low temperature, and aged membranes - requiring maximum feed pressure. Case 3 assesses minimum feed pressure under favorable conditions with new membranes. Case 4 examines maximum product TDS, testing compliance with quality standards under high salinity and temperature. Case 5 evaluates minimum product TDS, showcasing peak water quality under optimal conditions with new membranes and low feed TDS [208]. For the selected FSP RO configuration with no upper quality requirement, Cases 1 to 4 are particularly relevant (Table 6). These cases help define the operational pressure range for pump selection (Cases 2 and 3), assess the worst possible permeate quality to validate the system's reliability under extreme conditions (Case 4), and analyze operation under average conditions (Case 1) to determine OPEX. For alternative RO configurations, such as partial second pass (PSP) or split partial second pass (SPSP), design Case 5 becomes important as well to evaluate the maximum permeate bypass around the second RO stage.

The water quality obtained under worst-case conditions (Case 4) demonstrated that an FSP RO system alone cannot achieve the required water quality with a conductivity below 1 $\mu\text{S/cm}$. Even the occasionally reported less stringent conductivity requirement of up to 5 $\mu\text{S/cm}$ for AWE systems could not be met in any of the design cases. Consequently, incorporating a polishing stage downstream of the RO system became necessary.

For MWS1, two primary treatment options were considered: IEX and CEDI. CEDI was chosen due to its superior boron removal efficiency compared to conventional IEX [209–211]. The CEDI performance projection was based on the RO2 permeate quality from Case 4, aiming to determine whether the quality requirements could be achieved after the polishing stage. To maintain a conservative approach, a slightly lower boron rejection rate (80 %, instead of the projected 91 %) was applied. Nonetheless, as shown in Table 6, the projection indicates that the DI water quality not only meets but surpasses the ASTM Type II standard, with a TDS concentration of 0.12 mg/L and a resistivity of approximately 9.6 $\text{M}\Omega\cdot\text{cm}$. The ion species identified in the product stream were Na^+ (0.010 mg/L), Cl^- (0.016 mg/L), and boron (0.096 mg/L). Notably, all other ion concentrations present in the CEDI feed were reported to be $< 0.001 \text{ mg/L}$.

As described above, MWS2 includes an additional IEX mixed-bed polisher downstream of the CEDI to produce DI water in compliance with ASTM Type I standards. After the polisher, the thresholds for Na^+ and Cl^- concentrations of less than 0.005 mg/L, along with a conductivity exceeding 17.1 $\text{M}\Omega\cdot\text{cm}$ could be achieved. Boron thresholds are

Table 5
SWRO design cases adapted from [208].

Design case	TDS	Temperature	Membrane age
Case 1: Average conditions	→	→	→
Case 2: Maximum feed pressure	↑	↓	→
Case 3: Minimum feed pressure	↓	↑	↓
Case 4: Maximum product TDS	↑	↑	→
Case 5: Minimum product TDS	↓	↓	↓

Abbreviations: ↓ = Minimum value, → = Average value, ↑ = Maximum value.

DuPont conducted an investigation on one of their Type 1 SBA resins in OH⁻-form, exposing it to various temperatures over a 140 hour period. The remaining strongly basic groups were measured, revealing functional group losses of 2 % at 40 °C, 4 % at 50 °C, 6 % at 60 °C, 10 % at 70 °C, and 13 % at 80 °C [212]. These results highlight the significant influence of temperature on the thermal degradation of SBA resins. This degradation process can contribute to TOC accumulation in the DI loop, potentially affecting long-term system performance [140]. For this reason, DuPont recently introduced AmberLite™ P2 × 110, an ion exchange resin specifically designed for PEM applications. It is claimed to be suitable for operating temperatures of up to 70 °C, while also exhibiting low metal and TOC impurity leachables [213]. Other suppliers are likely to follow in the near future by developing resins designed to operate effectively at elevated temperatures as well.

To mitigate the negative effects of elevated temperatures, a heat exchanger is installed at the inlet of the DI purification system, ensuring that the operating temperature remains below 50 °C under all conditions. Downstream of the heat exchanger, a TOC-UV system operating at a wavelength of 185 nm is employed to degrade TOC, which is assumed to be present in the mid-μg/L range. The TOC-UV system converts TOC to CO₂ which is subsequently removed by the SBA resin in the IEX polisher mixed bed.

The mixed bed system is designed to operate at 40 bed volumes per hour (BVH) with a minimum resin bed depth of 1000 mm. The above presented AmberLite™ P2 × 110 UPW resin from DuPont in H⁺/OH⁻-form was selected as the resin type. The system design includes two GRP columns in series, each equipped with a dedicated set of valves to switch between bed positions and to isolate columns as needed. This setup provides full system redundancy, ensuring continuous operation even during resin replacement.

As the final step, a fine filter with a pore size of 0.2 μm is applied to remove any remaining particles in the DI loop. Additionally, online resistivity, and TOC measurements are considered for monitoring purposes. Beyond that, DI2 incorporates a second heat exchanger to pre-heat the treated water, given that treated water accounts for 50.0 % of the total DI loop flow rate at the stack array level. Without pre-heating, the lower temperature of the treated water could disrupt the module's heat balance, causing significant temperature gradients between the stack inlet and outlet. However, this potential issue is highly dependent on the specific heat balance at the respective stack array level and must be evaluated on a case-by-case basis.

Both system designs feature full redundancy for the TOC-UV system, IEX mixed beds, and fine filters. However, redundancy is not implemented for the heat exchangers, as they are highly reliable, not prone to malfunction, and require minimal maintenance. Redundant measuring devices are included only in DI2. The selected interconnecting pipework material is stainless steel with a PREN > 20 (e.g., 1.4404), ensuring suitability for the specified operating conditions.

7. Conclusion and outlook

This study assessed the technical feasibility of using seawater for large-scale green hydrogen production, identifying the most promising technologies for system design and water treatment integration. Key challenges and future research directions were outlined to enhance water treatment strategies and electrolyzer technologies, optimizing their integration for green hydrogen production. The primary water treatment related findings and recommendations are summarized below:

- The challenges of direct seawater electrolysis include cathode and anode side reactions, poor ionic conductivity of natural seawater, and the precipitation of Ca(OH)₂ and Mg(OH)₂ on the cathode surface [29,214]. Recent advancements, such as Lewis acid coatings and polyanion layers, have shown potential in improving reaction kinetics and mitigating chlorine-induced degradation, addressing key

CER-related challenges. However, the technology remains in its early development stages, further research is needed to overcome these limitations and establish seawater electrolysis as a competitive and scalable alternative [12,28,215]. Therefore, future research should target the integration of advanced protective coatings with scalable catalyst and reactor designs to enable practical seawater electrolysis.

- As large-scale electrolyzer deployment progresses, the effects of impurities on performance, durability, and cost remain insufficiently understood. In PEM electrolysis, research has primarily focused on selected cation species, while anionic impurities, particularly chloride, have received more attention, though the long-term impact of chlorine evolution at low concentrations remains unclear. The effects of organic contaminants are largely inferred from alcohol-fed systems [105]. While AWEs demonstrate long-term stability, impurity tolerance in modern high-performance configurations is not well established, raising questions about the necessity of strict water purity [105]. The role of boron as an impurity in both PEM and AWE systems also remains unclear, despite its relevance in seawater and the challenges associated with its removal. Most studies apply high impurity concentrations to accelerate degradation, yet real-world systems operate over extended periods with only trace-level exposure, underlining the need for long-term studies under realistic conditions [130]. Future research should prioritize systematic long-term testing of electrolyzers under realistic impurity levels to clarify tolerance thresholds, establish practical water treatment requirements, and ultimately guide the development of electrolyzers with reduced water purity demands.
- AST protocols reviewed in this work support the evaluation of degradation behavior in low-temperature electrolysis systems but primarily address operational stressors such as current density, temperature, and pressure. Water impurities remain underrepresented and are usually limited to a narrow set of ion species. Future work should focus on integrating defined impurity stressors, introduced individually or in mixtures, under controlled conditions to better assess their effects on performance and material degradation, and to enable meaningful comparisons across studies.
- Thermal desalination poses challenges for electrolyzer integration, requiring steady-state conditions and making water production highly dependent on electrolyzer performance. In contrast, SWRO operates independently, making it the preferred choice for large-scale green hydrogen production. A make-up water system using DMF, FSP RO, and CEDI, with TOC-UV and an IEX mixed bed for final polishing, was proposed. While these technologies are well-established with limited research potential, optimizing system integration is key to minimizing downtime and part-load operation based on electrolyzer load fluctuations. If future studies suggest less stringent water quality requirements, system configuration should be adjusted as well. Additionally, artificial intelligence offers promising potential for improving efficiency and reliability in water treatment through predictive analytics, real-time monitoring, and automated process optimization [216–218]. Efforts should focus on optimizing water treatment-electrolyzer integration and developing adaptive system configurations tailored to site-specific conditions to support effective planning and efficient system design. Further, the potential of artificial intelligence for improving operation and maintenance should be investigated, particularly its role in advanced system control, predicting component failures, and proactive scheduling to minimize downtime.
- A DI loop purification system for PEM electrolyzers was designed with TOC-UV and IEX as primary treatment steps. Research, primarily done by IEX resin suppliers like LANXESS and DuPont, focuses on optimizing system configuration for larger capacities to enable resin regenerability, reducing CAPEX and maintenance via economies of scale while also lowering OPEX by minimizing resin replacement costs [140,213]. Another key area is improving SBA resin stability, as degradation occurs above 40 °C, below typical PEM

operating temperatures. To address this, temperature regulation and additional cooling are required, while resin manufacturers are developing thermally stable Type 1 SBA resins capable of withstanding up to 70 °C [213]. A key priority is the development and validation of thermally stable SBA resins and optimized DI loop configurations that enable regenerability, reduce operating costs, and ensure long-term reliability in large-scale PEM electrolyzer systems.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the authors used Chat GPT to improve the readability and language of the manuscript. After using this service, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

CRedit authorship contribution statement

Andreas Augustin: Writing – original draft, Visualization, Methodology, Investigation, Conceptualization. **Thomas Wintgens:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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