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Review article

Proton exchange membrane water electrolyzers degradation models review: implications for power allocation and energy management

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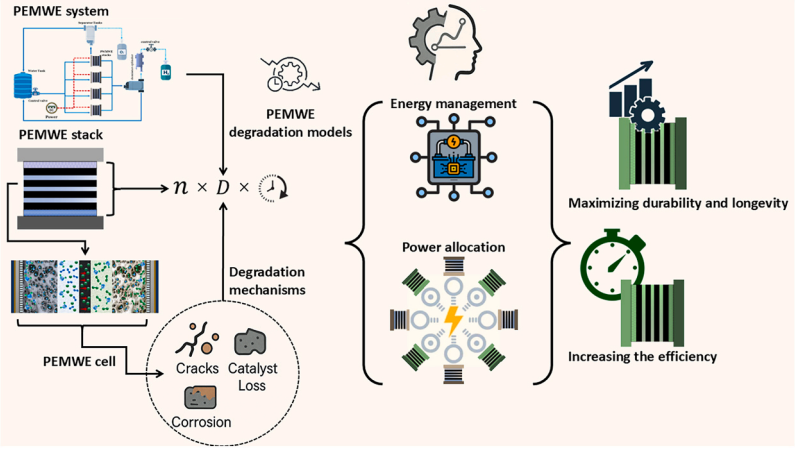
HIGHLIGHTS

- Investigation of PEMWE degradation models and their impact on energy management.
- Degradation mechanisms in membranes, catalysts, PTL, and BPPs are analyzed.
- Recent advancements in empirical, computational, and data-driven degradation modeling.
- Integration of advanced degradation models enables smarter power allocation in PEMWE.
- Practical strategies for extending PEMWE lifespan and improving efficiency.

GRAPHICAL ABSTRACT



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ABSTRACT

Proton Exchange Membrane Water Electrolyzers (PEMWEs) are pivotal in facilitating sustainable hydrogen production using renewable energy sources. Despite their operational efficiency and adaptability, PEMWEs experience significant performance challenges due to component degradation under dynamic conditions. The comprehensive analysis of degradation processes in PEMWE systems is the focus of this paper, which also highlights the use of empirical and sophisticated electrochemical degradation models in forecasting and controlling these impacts. Critical degradation mechanisms affecting membranes, catalyst layers, porous transport layers, and bipolar plates are analyzed comprehensively. The study additionally examines at how advanced degradation models might be included into power allocation and energy management plans, emphasizing the possibility of increased component lifespan and operational efficiency. Recent advancements in modeling techniques, from heuristic and optimization-based frameworks to data-driven approaches, are critically

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discussed. This combination of theoretical models and research highlights the importance of incorporating accurate degradation insights into real-time energy management systems, which will allow for more dependable, cost-effective, and financially feasible PEMWE installations. Ultimately, this review provides a foundational perspective for future innovations, emphasizing the necessity of embedding robust degradation modeling into sustainable hydrogen energy strategies.

1. Introduction

In the pursuit of sustainable energy solutions, hydrogen has emerged as an attractive energy vector due to its clean combustion, emitting only water vapor [1,2]. [3–9]It has been shown that a promising approach to sustainable Hydrogen Production (HyPro) utilizing renewable energy sources (RES) including solar, wind, and hydroelectric power can be achieved by electrolyzing water by various technologies. Electrolysis of water using proton exchange membranes (PEMWE) stands out as a reliable option as it provides rapid response times, acceptable efficiency, and compact structure [10,11]. PEMWE technology offers notable advantages, including high operational efficiencies, low-temperature operation, rapid response times, and the ability to operate under variable pressures, making it a versatile candidate for scalable hydrogen production systems [12–14].

Despite these benefits, significant challenges related to system costs, material stability, water quality requirements, and, critically, component degradation remain obstacles to widespread PEMWE adoption [15]. Degradation processes within PEMWE systems significantly affect their efficiency, reliability, and operational lifespan, necessitating a thorough investigation into their underlying mechanisms and appropriate mitigation strategies [16–18]. Although Electrochemical Degradation Models (DMs) provide valuable insights into degradation phenomena, their complexity and computational demands often restrict real-time applicability for effective energy management [19,20].

With the increasing capacity of PEMWE stacks production to meet the demand for sustainable HyPro, as illustrated in Fig. 1 [21], the scalability of PEMWE technology underscores the urgency of addressing degradation-related challenges [22]. The expansion of PEMWE installations enhances the significance of robust and accurate DMs in ensuring system reliability and performance over the long term, amidst predictions of continued growth [23]. The transition to larger-scale PEMWE systems introduces novel challenges, particularly in managing degradation impacts on system efficiency and durability. Consequently, a comprehensive understanding of degradation mechanisms and the application of precise DMs are indispensable for optimizing system performance and sustainability.

PEMWE degradation has been studied using a variety of modeling techniques, ranging from simple analytical methods to complex computational approaches [24]. The application of these insights within energy management and power allocation frameworks remains a notable challenge. This manuscript aims to bridge the gap between theoretical knowledge and practical applications of degradation phenomena to address this gap. To be more specific, this paper contributes by systematically analyzing degradation mechanisms, classifying existing degradation models, and identifying operational modes that significantly affect PEMWE performance. Further, the manuscript emphasizes the importance of integrating degradation considerations into practical energy management strategies so that the reliability and efficiency of PEMWE systems can be enhanced.

Section 2 describes critical PEMWE components as well as their vulnerability to degradation in this paper. Section 3 explains various PEMWE degradation models and illustrates the strengths and limitations of each model. Section 4 presents practical strategies for managing energy and allocating power so that performance losses can be mitigated by integrating degradation phenomena with energy management and power allocation. Finally, Section 5 synthesizes insights from the preceding sections and outlines future research directions aimed at advancing PEMWE technology toward broader sustainable energy adoption.

2. Critical components of PEMWE and their vulnerability

The PEMWE is an electrochemical device that splits water (H_2O) into hydrogen (H_2) and oxygen (O_2) gases using electricity. This process involves water oxidation at the anode, which produces O_2 and isolated hydrogen ions (H_+). At the cathode, H_+ (protons) combine with electrons (e_-) from an external circuit to produce hydrogen gas. A PEM separates these compartments, allowing protons to migrate while blocking electrons. These reactions take place in separate compartments divided by a PEM. Once the current has been applied to the PEMWE, water molecules lose e_- at the anode while protons move to the cathode

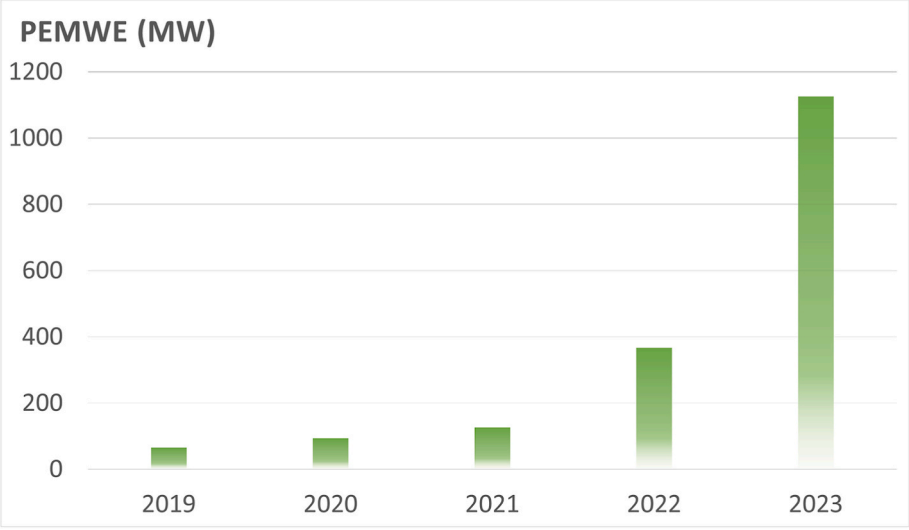

Fig. 1. Growing trend of installed capacity of PEMWE stacks.

through the membrane. As a result of the combination of protons and electrons at the cathode, hydrogen gas is formed. Using the PEM, gas separation can be achieved, which enables hydrogen gas to be collected as the desired product, while oxygen gas is typically released as a byproduct. Overall, the PEMWE facilitates the efficient and controlled production of hydrogen gas through electrochemical water splitting [25].

A PEMWE structure consists of a stack made of multiple units of cells. Fig. 2 shows a PEMWE stack and its structural configuration. The stack consists of four individual cells, distinctly numbered. The positive and negative sides of the stack are explicitly marked with plus and minus symbols. One specific cell is meticulously zoomed in to enhance the comprehension of internal dynamics within a PEMWE cell, presenting a schematic representation. Various layers are demonstrated, and material transfer is represented.

In PEMWEs, the membrane electrode assembly (MEA), CL, Porous Transport Layers (PTLs), and bipolar plates (BPPs) with flow channels make up the assembly (Fig. 2). Among these components, the PTL is vital in optimizing the PEMWE system by facilitating improved utilization of the CL. The PTL serves as a conduit for efficiently transporting reactant gases and facilitates the distribution of reactants across the CL. PTL is often referred to as a gas diffusion layers (GDL). Its porous structure allows for enhanced mass transfer, ensuring effective utilization of the catalyst material and promoting uniform electrochemical reactions [26]. The current collectors, positioned between the external circuit and the flow-field plates (or flow channels) (see Fig. 2), are essential for distributing current uniformly and ensuring effective electrical contact with the catalyst layer. End plates are positioned at both ends of the stack to apply uniform mechanical pressure, maintain sealing integrity, and ensure stable operation under pressurized conditions. By providing a favorable environment for gas diffusion and maintaining sufficient contact with the CL, the PTL contributes to the overall performance and efficiency of PEMWEs. This intricate interplay between the PTL and CL highlights the significance of their interaction in achieving optimized electrolysis processes in PEMWEs [27,28].

In a PEMWE cell, electrolysis occurs by delivering water to the anode, dissociating into O_2, H_+, and e_-. The following equations can express the reactions taking place in a PEMWE. The overall reaction representing the electrochemical splitting of water into hydrogen and oxygen is depicted in Equation (1). It is important to note that this reaction occurs at the respective electrodes, with the anode responsible for oxygen evolution reaction (OER), as shown in Equation (2), and the cathode facilitating hydrogen evolution reaction (HER), as depicted in Equation (3) [29].

$$2H_2O \rightarrow O_2 + 2H_2 \quad (1)$$

$$2H_2O \rightarrow O_2 + 4H_{(+)} + 4e_{(-)} \quad (2)$$

$$4H_{(+)} + 4e_{(-)} \rightarrow 2H_2 \quad (3)$$

As described and shown in Fig. 2, a PEMWE cell, the layered structure, can be segmented into various components, each serving a specific function. The division of a PEMWE into these distinct layers and components allows for the precise management of reactants, efficient ion transfer, and effective separation of product gases. This intricate design is critical in optimizing PEMWE systems' performance and efficiency. However, despite their significance, these fundamental components are susceptible to diverse forms of degradation [30,31]. For further investigation of degradation factors, the primary components can be divided as follows: *membrane, CLs, PTL, and end plates.*

2.1. Membrane

Membrane in PEMWEs serves as a critical component that allows the migration of protons while preventing the passage of electrons. It plays a vital role in maintaining reactant gas separation and facilitating ion transfer during the electrolysis process [32]. Membrane degradation in PEMWEs can be classified into mechanical, chemical, and thermal degradation mechanisms. Mechanical degradation is typically associated with early failures caused by mechanical stresses, inadequate humidification, and structural issues such as punctures, tears, and cracks. Chemical degradation occurs due to the attack of oxidizing species and metallic ions, resulting in chain scission, loss of functional groups, and reduced ionic conductivity. Thermal degradation involves the removal of sulfonic acid molecules from the membrane and is triggered by elevated temperatures [33].

To investigate the effects of temperature and current density on membrane degradation, Chandesris et al. [34] developed a 1D model.

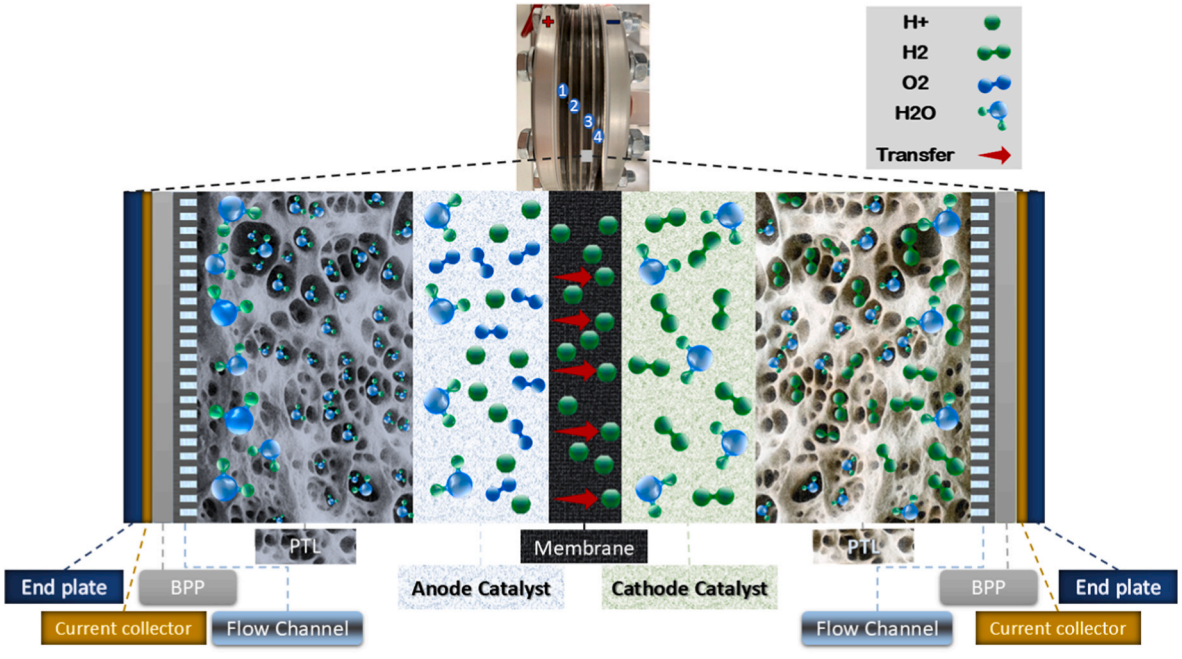

Fig. 2. Degradation-prone components of a PEMWE

Their experimental findings confirmed that degradation primarily occurs on the cathode side and revealed the significant influence of temperature. The model effectively captured the complex relationship between current density and degradation rate, including a maximum at low current density. Furthermore, it accurately predicted the observed accelerated thinning of the membrane over time.

In the EU ELECTROHYPEM, Siracusano et al. [35] investigated the degradation mechanisms affecting MEAs and stack components in PEMWEs to achieve long-term durability exceeding 100,000 h. A demonstration stack incorporating these optimized components was tested for 3500 to 5700 h under real-life operating conditions. Through a combination of electrochemical and physico-chemical techniques, the study identified key degradation pathways and evaluated the endurance of the MEAs. Further, it is important to note that the development of more advanced components represents a distinct and complementary strategy for improving PEMWE performance and durability.

In their comprehensive review, Chen et al. [36] addressed the advancements and challenges in PEMWE technology, emphasizing key components and their impact on performance. They highlighted the critical importance of high-performance electrocatalysts and long-term stability in PEMWEs. Additionally, they discussed strategies such as using composite materials and 3D printing to enhance the membrane and BPPs. The review offers valuable insights and directions for future research and development in PEMWEs.

2.2. Catalyst layer

Catalyst degradation in the CL of PEMWEs can have a detrimental impact on performance over time. This degradation can occur through the dissolution of catalyst materials, such as iridium and platinum, during operation. Passivation of the anode support can impede current flow, while agglomeration of catalyst particles can result in a loss of electrochemical surface area [37]. Additionally, metallic cations can poison the catalyst, leading to increased charge transfer resistance and reduced reactivity [38]. In their mini-review, Pushkarev et al. highlight the importance of PEMWE for efficient and practical green HyPro. They emphasize the significance of OER electrocatalysts, particularly those based on noble metals like Ir or Ru, in determining the efficiency and stability of water splitting [39].

The cathode CL is responsible for HER, where protons from the membrane combine with electrons to form hydrogen gas. Similarly, the anode CL facilitates OER, where water molecules are oxidized, producing oxygen gas, protons, and electrons. Catalyst degradation in these layers can be caused by contamination, corrosion phenomena, or agglomeration of catalyst particles, resulting in reduced catalytic activity and compromised system performance [40,41].

The integration of empirical findings, such as degradation rates obtained from accelerated stress testing (AST), into PEMWE models, marks a significant enhancement in their predictive accuracy. For example, findings that detail membrane thinning at 0.1 μm per 1000 h and a 20 % reduction in catalyst active surface area over 500 h under certain conditions, provide invaluable insights into power allocation and energy management within PEMWE systems [42]. This quantitative approach is vital for the development of robust models that can accurately forecast system performance under varying operational scenarios. Highlighting the work of Feng et al., the literature underscores the crucial role of understanding degradation mechanisms affecting electrocatalysts and CLs, such as dissolution, poisoning, agglomeration, and migration. These factors critically influence PEMWE's performance and durability, emphasizing the necessity for advanced mitigation strategies, including the optimization of catalyst supports and layer structures [43]. In their research on PEM water electrolysis, Pham et al. focus on optimizing catalyst materials and electrode structure to mitigate degradation and reduce the use of noble metals. They emphasize the importance of a holistic approach that considers all components of the electrode to enhance performance and durability. The study highlights the promising results achieved with supported iridium oxide catalysts, which exhibit improved dispersion and performance at low loadings. Critical parameters such as ionomer content, porosity, and interfacial contact are identified as significant factors in designing an optimal anodic electrode with low iridium loading. These findings offer valuable insights for future research and development aimed at addressing degradation and cost reduction challenges, with the goal of achieving widespread adoption of PEMWE technology [44]. Mirshekari et al. [45] presents a pioneering study on high-performance, cost-effective membranes for PEMWEs and ensures precise control and distribution of the catalyst composition and loading. Utilizing reactive spray deposition technology, the fabricated MEAs demonstrate exceptional durability and activity with significantly reduced platinum group metal (PGM) loadings. These findings have promising implications for commercializing PEMWEs, with future research focusing on scaling up MEAs and optimizing the Pt recombination layer to further improve performance and reduce hydrogen cross-over.

Yu et al. conducted a comprehensive study on the degradation of a PEMWE with ultra-low catalyst loading. After a long-term test lasting 4500 h, they proposed a mechanism for cathode degradation, involving the dissolution of platinum from nanoparticles and rapid reduction of platinum oxide. The analysis revealed that iridium dissolution and redeposition were responsible for a significant portion of anode catalyst loss. Additionally, the distribution of platinum and iridium across the MEA was quantified, highlighting the formation of Pt-Ir precipitates in the membrane. These findings provide valuable insights into the degradation mechanisms and behavior of platinum and iridium in PEM water electrolysis systems [46].

Suermann et al. propose an electrochemical characterization protocol to investigate degradation factors in PEM water electrolyzers. They identify apparent degradation resulting from changes in catalyst oxidation states, as well as real degradation at the ohmic and mass transport overpotentials, particularly under higher current densities and longer operating times. This study offers valuable insights for the development of ASTs and the understanding of fundamental degradation mechanisms in PEM water electrolyzers [47]. Li et al. conducted a theoretical analysis demonstrating that operating PEM water electrolyzers under boiling conditions can significantly reduce electrolysis voltage compared to non-boiling and gas-phase conditions, suggesting a potential strategy for enhancing system efficiency [48].

2.3. PTL

The PTLs play a crucial role in PEMWEs by facilitating reactant gas transport and ensuring optimal utilization and reaction rates within the CLs. In addition, these layers help dissipate excess water generated during the electrolysis process [49].

Yuan et al. provide a comprehensive review of the PTL in PEMWEs, underscoring its significance in achieving stable electrochemical performance. The authors discuss different types of PTLs and their properties, with particular emphasis on the PTL/CL interface and its impact on overpotentials. The study investigates the influence of PTL microstructure on kinetic, ohmic, and mass transport overpotentials, providing a valuable resource for material development and quality control. The authors also emphasize the need for further research on PTL materials, interfacial properties, systematic studies, and corrosion effects to optimize PTL design and advance PEMWE technology [50]. A recent 2000 h comparison of seven Ti-based coatings confirms that iridium-doped SnO_2 remains the most corrosion-resistant option, while several PGM-free nitride layers already meet the $\leq$10 μV h^{-1} target under 2 A cm^{-2} operation [51].

Stiber et al. developed a PTL for PEMWE, specifically the porous sintered layer (PSL) on a low-cost titanium mesh (PSL/mesh-PTL). This novel design enabled operation at high current density (up to 6 A cm−2), elevated temperature (90 °C), and increased hydrogen output pressure (90 bar). Compared to the mesh-PTL alone, the PEMWE

incorporating the PSL/mesh-PTL achieved the same cell potential but at a higher current density, resulting in 31 % higher efficiency at a nominal load of 4 A cm−2. Pore network modeling demonstrated that the PSL/mesh-PTL design facilitated efficient gas and water management, eliminating the need for a complex flow field in the BPP. These findings not only enhance the economic attractiveness of PEMWE but also pave the way for large-scale integration of renewable energies with reduced CO2 emissions. The PSL/mesh-PTL developed in this study is now commercially available for interested laboratories to order from GKN Sinter Metals [52].

Rakousky et al. [53] focus on significant role of the anode's PTL and its surface condition on PEM electrolyzer performance. The document highlights that utilizing Pt-coated titanium PTLs substantially mitigates degradation, cutting down the rate to 12 mV/h compared to 194 mV/h with uncoated PTLs, primarily by preventing titanium passivation. This underscores the importance of surface coatings on PTLs for enhancing the durability and efficiency of PEM electrolyzers, suggesting a strategic approach to selecting and designing PTL materials to curb degradation rates effectively.

2.4. Bipolar plates and current collectors

Electrode/electrolyte interfaces in PEMWEs are susceptible to degradation, adversely affecting system performance and shortening lifespan. This degradation can manifest as electrochemical reactions, delamination events, or accumulation of reaction byproducts [46].

BPPs used in PEMWEs are particularly prone to hydrogen embrittlement, passivation, and corrosion. Titanium BPPs require additional coatings to enhance their durability due to their susceptibility to hydrogen embrittlement and passivation. This is primarily due to the spontaneous formation of a passive TiO_2 layer under high anodic potentials, which significantly increases interfacial resistance and diminishes electrical performance; protective coatings are therefore necessary to mitigate these effects and ensure long-term conductivity [54]. Corrosion can also occur due to chemical attacks from fluoride ions and hydrogen peroxide [55]. Prestat's analysis underscores the complexity of corrosion phenomena within PEMWE anodes, particularly concerning BPPs and PTL, traditionally comprised of titanium. Prestat's review elucidates the progression towards employing less costly materials, such as stainless steel, contingent on the development of effective protective coatings against the harsh oxidizing environment within the anode compartment [56].

A comprehensive analysis by Teuku et al. highlights the crucial role of BPP materials and fabrication methods in achieving optimal performance and durability in low-temperature PEMWEs. The review emphasizes the importance of corrosion and interfacial contact resistance and calls for innovative solutions to address these challenges. Recent studies have demonstrated that coatings of iridium (Ir), boron nitride (BN), and tantalum (Ta) on titanium BPPs significantly enhance corrosion resistance and overall performance in PEMWEs, highlighting their potential for improving system durability and efficiency [57–60]. Notably, coating materials such as Ir, Nb, and Ta have shown promising outcomes in maintaining low interfacial contact resistance. Additionally, emerging techniques like metal 3D printing offer exciting possibilities for the cost-effective production of BPPs and corrosion mitigation in PEMWEs [61].

The shape of end plates also influences production and durability in PEMWEs. Jo et al. compared circular and square end plates in a highly pressurized PEMWE stack. They successfully designed lightweight end plates through finite element analysis and topology optimization, achieving weight reductions of 22.9 % and 23.3 % for circular and square end plates, respectively. Importantly, their analysis confirmed that the uniformity of clamping pressure was maintained in both end plate designs, thereby enhancing the performance of high-pressure PEMWE systems by ensuring gas-tight sealing and uniform pressure distribution [62].

In addition to BPPs, current collectors in PEMWEs, typically made of titanium, can undergo chemical degradation leading to passivation and corrosion. Mechanical degradation can also occur due to compression pressures that affect the properties of the current collectors and their interfaces with the CLs and BPPs. Compression pressure significantly influences mass transport, current transport, and overall cell performance [63].

To encapsulate the intricate dynamics of degradation across different components of PEMWEs and the innovative strategies devised to counteract these effects, Table 1 provides a succinct overview, underlining the mechanisms, pivotal discoveries, and significant contributions from various studies.

3. Modeling of PEMWE degradation

Understanding the precise degradation mechanisms of PEMWE components is crucial for developing models and consequently effective EMSs. Recent empirical research and theoretical methods for describing degradation processes and its operational effects are described in this section. Accurate degradation modeling is particularly vital as it enables system designers and operators to anticipate performance losses due to factors such as intermittent renewable power inputs, fluctuating temperatures, and varying pressures. Critical factors such as electrical supply [64], suboptimal water management, elevated pressures [65], and high operating temperatures can significantly undermine the performance and longevity of PEMWE systems. AST protocols summarised by Urbano et al. [66] systematically link specific stressors (temperature, power-cycling amplitude and water-flow rate) to distinct voltage-loss signatures, providing a valuable empirical bridge between short-term AST data and long-term degradation models. A recent state-of-the-art survey by Wolf et al. [67] collates four decades of stack-level evidence, ranking catalyst dissolution, membrane chemical attack and PTL corrosion as the dominant voltage-loss drivers and mapping the diagnostic methods that quantify each pathway—providing the baseline for the mechanisms illustrated in Fig. 3.

The distribution of water plays an essential role in maintaining PEMWE efficiency and mitigating component damage. A study by Frensch et al. [68] analyzed seven operation modes, including constant current and voltage, alongside current cycling, revealing that rapid current cycling enhances cell performance through ohmic resistance reduction. However, dynamic operations were associated with increased fluoride emissions and membrane thinning, highlighting the need for judicious operation mode selection and the development of strategies to foster efficient, durable PEMWE systems. Bazarah et al. contribute to the discourse by exploring how both static and dynamic factors, including stack design and operating conditions, affect PEMWE performance and durability. The review advocates innovative approaches like 3D printing and hydraulic cell compression to enhance electrolyzer efficiency, highlighting the importance of temperature, pressure, and water flow rate in system optimization [69].

Various analyses have been performed on degradation phenomena at both the micro- and macroscale, ranging from the integrity of cell components under various stresses to the performance of stacks and systems. Such comprehensive evaluations aim to elucidate the degradation processes affecting the membrane, CLs, and GDL, alongside the broader system-level operational strategies [70,71]. PEMWE production systems require an intensified focus on DMs to maximize efficiency and longevity. These models offer insights into degradation mechanisms such as catalyst deterioration [72], membrane ageing [73], electrode/electrolyte interface issues [74], and water management challenges. Accurately capturing degradation processes facilitates proactive measures to minimize degradation effects and ensure optimal system performance. Research by Garbe et al. [75] focused on the impact of high-temperature conditions, observing that PEMWE cell operation at 100 °C led to a quicker rate of voltage loss and accelerated degradation compared to lower temperature operations. The study underscores the

Table 1
Summary of degradation mechanisms and key findings in PEMWE components.

Component	Main materials	Degradation mechanisms	Related features affecting degradation	Key findings	Ref.
Membrane	Perfluorosulfonic acid (PFSA) (e.g., Nafion), composite membranes	Mechanical, Chemical, Thermal	Thickness, ionic conductivity, water content, operation temperature	+Degradation occurs mainly on cathode side +Effects of temperature and current density significant +Development of components enhancing durability and performance +High-performance, cost-effective membranes developed	[32–36, 45]
CL	Anode: Ir, IrOx, RuOx; Cathode: Pt, Pt/C, supported IrO_2	Dissolution, Passivation, Agglomeration, Poisoning	Catalyst support material, loading, dispersion, ionomer content, particle size	+Degradation impacts performance over time +Optimization of catalyst materials and electrode structure critical +Supported iridium oxide catalysts show improved dispersion and performance +Pt and Ir degradation mechanisms identified	[38–41, 44,46,47]
PTL/GDL	Ti mesh, Ti felt, Pt-coated Ti, SnO_2-doped Ti, PGM-free nitrides	Corrosion, Passivation, Mechanical Stress	Porosity, coating material, thickness, microstructure, interfacial properties	+Facilitates reactant gas transport and optimal utilization within CLs +PSL/mesh-PTL design enhances gas and water management +Pt-coated titanium PTLs reduce degradation rate.	[49,50,52, 53]
BPP	Ti (uncoated, Ir/Ta/Nb/BN-coated), SS (coated), carbon-based, 3D printed metals	Corrosion, Hydrogen Embrittlement, Passivation	Coating type, fabrication method, interfacial resistance, flow field geometry	+Titanium BPPs require coatings for durability +Shape and material of end plates influence production and durability +Innovative solutions and materials for BPPs and end plates can enhance performance.	[55, 61–63]
Current collectors	Ti, coated Ti, SS (with protective coatings)	Corrosion, Passivation, Mechanical Compression	Compression pressure, coating, interface quality	+Titanium collectors degrade under high pressure and oxidation +Compression affects electrical contact and transport phenomena +Material stability and surface treatments improve performance	[63]

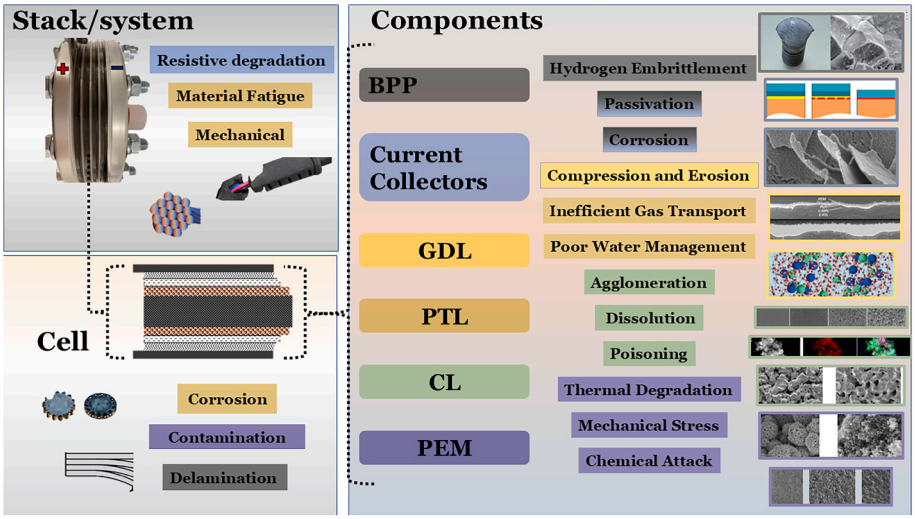

Fig. 3. Degradation mechanisms in PEMWE.

necessity for meticulous temperature regulation to leverage efficiency improvements against the backdrop of increased degradation risks.

Aβmann et al. [76] contributed insights into the primary degradation mechanisms within PEMWEs, such as anode catalyst dissolution, membrane chemical decomposition, and semiconducting oxides formation on metal components. These processes are exacerbated by conditions like high current density and dynamic operation, prompting the recommendation of AST protocols for evaluating the durability of emerging, cost-effective components and the importance of standardized testing hardware for reliable component evaluation.

The degradation of current collectors, essential for CL contact, is categorized into chemical and mechanical processes, highlighting the susceptibility of stack metallic components to degradation under pressure. The systematic examination of these mechanisms is crucial for

ensuring the long-term operation and durability of PEMWEs. Fig. 3 delineates the potential degradation mechanisms within various components of PEMWEs, including the stack, cells, and layers, illustrating the complex interplay of factors that compromise system integrity.

Understanding the vulnerabilities and degradation mechanisms of PEMWE components—encompassing electrodes, membrane, catalysts, transport layers, flow channels, and BPPs—is pivotal for advancing system durability and efficiency. Strategies encompassing effective mitigation measures, material optimization, and sophisticated monitoring systems are essential for bolstering PEMWE performance and reliability. The forthcoming discussion on DMs aims to further elucidate these processes, fostering the development of precise maintenance strategies for sustaining PEMWE systems' performance over time.

3.1. Thermodynamics and operational principles of PEMWE

As it was discussed in first Section and shown in equation (1), PEMWE splits water into hydrogen and oxygen. The water-splitting process requires energy input, typically supplied by electricity, to drive the electrolysis reaction. By considering the maximum heat energy input (48.6 kJ/mol), the resulting reversible cell voltage "V_{rev}" can be calculated, as described in Eq. (4).

$$V_{rev} = \frac{\Delta G}{n_e.F} = 1.23\ V \tag{4}$$

$$\Delta H = \Delta G + T\Delta S \tag{5}$$

Here "ΔG" is Gibbs free energy which means the change in Gibbs free enthalpy and equals $237.22\left(kJmol^{-1}\right)$. Temperature is shown by "T" and expressed in Kelvin. "ΔS" is the entropy of the reaction. "F" stands for Faraday's constant and is 96500 (C mol^{-1}). The quantity of involved electrons is also "n_e" [77]. Although, during the water-splitting process, entropy is generated inevitably, making it more appropriate to use enthalpy "ΔH" (5) instead of "ΔG" for potential calculations. Consequently, under standard conditions, the change in enthalpy is 285.84 $kJ\ mol^{-1}$. Therefore, we can calculate the minimum voltage required "V_{th}" for water electrolysis using Eq. (6) which represents the thermoneutral voltage.

$$V_{th} = \frac{\Delta H}{n_e.F} = 1.48\ V \tag{6}$$

It's worth noting that the thermal energy used in Eq. (4), also referred to as the Lower Heating Value (LHV), and the thermal energy expression in equation (6), known as the Higher Heating Value (HHV), play important roles in the calculations.

To accurately determine cell voltage "V_{cell}" and account for various losses, including thermoneutral voltage, additional considerations are needed. The main contributors to increased voltage in a PEMWE can be classified into three major categories as shown in (7): Ohmic losses "U_o", activation losses "U_a", and concentration losses "U_C". In some cases, however, only activation and ohmic losses are considered for purposes of simplifying the modeling process. Polarization curves, which depict the relationship between cell voltages and current densities, are commonly used to compare electrolysis cell performance as shown in Fig. 4 [78].

$$V_{cell} = V_{th} + U_a + U_o + U_C \tag{7}$$

In accordance with the fundamental principle of energy conservation described by the first law of thermodynamics, the conversion efficiency is determined by quantifying the amount of electrical energy converted into chemical energy. Understanding the efficiency of a PEMWE system is essential, as reductions in efficiency often indicate underlying degradation mechanisms; thus, evaluating efficiency serves both as a degradation diagnostic and as a validation parameter for electrochemical models. Water electrolysis efficiency is assessed using hydrogen HHV. Considering that water is supplied to the electrolysis cell in its liquid phase, the efficiency can be calculated using equation (8) provided below.

$$\eta_{el} = V_{th}/V_{cell} \times 100 \tag{8}$$

Consequently, the efficiency of a water electrolyzer can be calculated by a given current density for any given size of electrolyser.

In PEMWE, faradaic efficiency is one of the quantitative analyses which is useful in determining how many electrons are transported in the external circuit to the surface of the electrode for conducting the electrochemical reaction either OER or HER and other electrochemical reactions in the electrolytes. Therefore, the faradaic efficiency can be defined as the ratio between the experimentally evolved volume of gas value (hydrogen or oxygen) and the theoretically calculated volume of gas value, as shown in Eq. (9). The theoretical gas volume generated during electrolysis can be determined using Faraday's second law, considering the current density, electrolysis time, and electrode area. This is done assuming 100 % Faradic efficiency, as described in Eq. (10). The actual amount of gas produced in experimental settings can be measured using techniques such as the water-gas displacement method or gas chromatography analysis.

$$\eta_F = V_{HyPro}/V_{Hcal} \times 100 \tag{9}$$

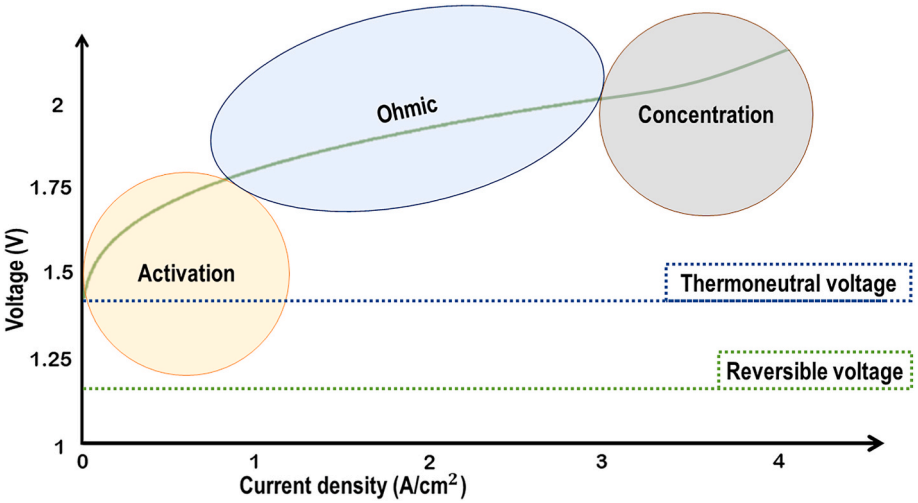

Fig. 4. PEMWE cell polarization curve.

$$V_{Hcal} = \frac{V_M . I . t}{2F} \quad (10)$$

$$V_M = \frac{R(273 + T)}{P} \quad (11)$$

Where "V_{Hcal}" shows the theoretically calculated H_2 volume. It can be calculated by Eq.(10) and "V_M" which stands for molar volume of the gas ($Lmol^{-1}$), is the outcome of Eq.(11). "t" is time in seconds, and current is shown by "I" and in amperes (A). "T" denotes the temperature. The symbol R represents the ideal gas constant (0.0821 $atm.K^{-1}.mol^{-1}$), where "P" represents the pressure in units of atm, and F corresponds to Faraday's constant (96,485 $C{\cdot}mol^{-1}$)[79,80].

Yodwong et al. [81] focused on analyzing and modeling Faraday's efficiency in PEMWE based on variations in current density and hydrogen pressure. The results demonstrate that Faradaic losses are significant at low current densities. An increase in hydrogen pressure leads to a decrease in Faraday's efficiency. The findings highlight the importance of further research to investigate the model coefficients for different PEMWE and to thoroughly understand the impact of the high-pressure operation on Faraday's efficiency, thus providing valuable insights for optimizing electrolyzer efficiency in varying operating conditions.

Finally, the energy efficiency of the system, which is widely used in energy management and power allocation, can be calculated from (12) by determining the ratio between productive energy and input energy.

$$\eta_s = E_{HyPro} / E_{input} \times 100 \quad (12)$$

"E_{HyPro}" is productive energy, which represents the amount of hydrogen produced per unit of time, and its HHV. On the other hand, "E_{input}" stands for the input energy the multiplication of input voltage and current in terms of time. This efficiency calculation provides valuable insights into the system's ability to efficiently convert input energy into useable hydrogen energy. This makes it a crucial metric in evaluating its overall performance and utilization [82].

The overall energy efficiency of the PEMWE system can be determined by multiplying the individual efficiencies of different components as illustrated in Eq. (13). This includes cell voltage efficiency and Faraday efficiency. Additionally, the efficiency of auxiliary equipment specific to each system should also be considered.

$$\eta_{PS} = \eta_{el} \times \eta_F \times \eta_{au} \quad (13)$$

A PEMWE system's overall energy efficiency, denoted as "η_{PS}", is determined by the product of multiple individual efficiencies. One of these efficiencies is cell voltage efficiency, "η_{el}". This reflects the cell's effectiveness in converting electrical energy into chemical energy (Eq. (8)). Another important efficiency is the Faraday efficiency, "η_F", which accounts for losses resulting from gas diffusion and is closely associated with the operating pressure, p. It quantifies the extent to which the actual amount of hydrogen produced matches the theoretical amount based on Faraday's laws. Additionally, system energy efficiency should consider auxiliary equipment, "η_{au}". This is specific to each system and contributes to overall performance and energy utilization [83].

3.2. Component degradation: modeling and mitigation strategies

Electrochemical models for degradation inherently involve the analysis of in situ components, wherein the degradation of specific elements plays a critical role. When it comes to PEMWE, degradation of the membrane is of the utmost importance due to its significant impact on system performance and durability. Understanding the mechanisms and factors contributing to membrane degradation is essential for developing accurate and reliable electrochemical models that can effectively predict and mitigate degradation effects in PEMWE systems.

Chandesris et al. [34] investigated the influence of temperature and current density on chemical degradation rate. They found that membrane degradation primarily occurred on the cathode side and observed a significant increase in chemical degradation with increasing temperature. The effect of current density was more complex, with a maximum degradation rate observed at low current densities. A 1D PEMWE model incorporating degradation mechanisms was developed, successfully capturing the temperature and current density effects on degradation rates. This included unexpected behavior at low current densities. The model was further utilized to analyze the time evolution of membrane thickness under constant current density, demonstrating the acceleration of degradation over time. Equation (14) describes the temporal changes in the membrane thickness within the model. As the membrane thins, the oxygen crossover intensifies, resulting in an accelerated fluoride release and membrane degradation. Consequently, the membrane thinning process is expected to follow an exponential rather than linear time evolution, due to this acceleration.

$$\frac{d\delta_M}{d_t} = \Delta\delta_M R_f \quad (14)$$

"$\Delta\delta_M$" in this equation refers to the reduction in membrane thickness per mole of released fluoride. "R_f" represents the rate of fluoride release in moles per second, obtained from the membrane DM. To address the issue of modeling membrane thinning and its associated geometric changes, the research study implemented a change of variable in the spatial parameter "X". This variable represents the direction of membrane thickness as shown in Eq. (15). "δ_M^0" in this equation demonstrates the membrane thickness at time zero.

$$X = \frac{\delta_M}{\delta_M^0} X_0 \quad (15)$$

This approach allowed for an effective representation of evolving membrane structure and its influence on overall system dynamics. The methodology employed in the study enabled the researchers to overcome the challenge of incorporating membrane geometry changes into the modeling process.

Sánchez Batalla et al. [84] analyzed the degradation behavior of a 3D-printed Ti6Al4V porous transport electrode with minimal precious-metal loadings (0.26 mg Ir cm^{-2} anode and 0.28 mg Pt cm^{-2} cathode). In their study, conducted at mild conditions (60 °C and 15 mA cm2 in 1 M H2SO4), Ir and Ti/V dissolution dominated the initial rapid degradation at the beginning, which then was followed by ionic resistance growth in the contaminated catalyst layers after 100 h. Remarkably, switching to deionized water operation (80 °C, 100 mA cm^{-2}) substantially mitigated degradation rates seven-fold. These findings underscore the critical influence of electrolyte purity and catalyst loading on catalyst longevity, advocating the necessity to parameterize these factors in predictive degradation models.

Padgett et al. [85] extended these findings with a comprehensive 4000-h durability test at significantly higher current densities (3 A cm^{-2}) using ultra-low precious-metal loadings (0.4 mg Ir cm^{-2} anode, 0.1 mg Pt cm^{-2} cathode). Using galvanostatic Electrochemical Impedance Spectroscopy (EIS), post-mortem Scanning Transmission Electron Microscopy with Energy Dispersive X-ray Spectroscopy (STEM/EDS), and periodic polarization measurements, they successfully separated degradation into four main components: catalyst activity loss (27 %), catalyst-layer resistance growth (19 %), residual unknown mechanisms (11 %), and Ir dissolution (43 %). Their methodical approach provides robust, transferable parameters crucial for enhancing the fidelity of physics-based and data-driven catalyst degradation models, particularly relevant under high-current, low-PGM regimes.

To further improve catalyst stability, Hernández-Castillo and Exner [86] presented a unique ripening-induced embedding technique that anchors iridium nanoparticles in a CeO_2 matrix to prevent agglomeration and dissolution. With a low Ir loading of 0.30 mg cm2, they were able to sustain three amps per square centimeter at only 1.72 V for an

extended period of 6000 h, with a degradation rate of only 1.33 V per hour. Their method not only outperforms the 2026 durability goal set by the U.S. Department of Energy, but it also provides useful coefficients that may be used as standards and useful inputs to improve current catalyst-aging models.

Chang Domínguez et al. [87] combine a mechanistic Ir-dissolution model with a temporal multiscale algorithm that decouples sub-second transport/kinetic oscillations from the hour-scale loss of electro-chemical surface area. By solving only one quasi-period of the fast dynamics per slow time step, they compress a 21-day durability simulation into ~20 min—about 1000 × faster than a fully resolved integration—while keeping the mean-squared error below 10-5. This white-box framework therefore opens a practical path for physics-grounded, real-time prediction of catalyst ageing under dynamic load profiles.

Complementing these catalyst-centric studies, a detailed investigation by Zeng et al. [88] employed Reactive Spray Deposition Technology (RSDT) to fabricate an 86 cm^2 MEA with ultra-low precious-metal loadings (0.2–0.3 mg(PGM) cm^{-2}), tested over 5000 h. According to their investigation, Pt migration at the cathode was negligible, but Ir dissolution and re-deposition were the main degradation processes, responsible for more than 70 % of the voltage rise. For the purpose of parameterising catalyst dissolution and redeposition processes in predictive degradation models, this spatially-resolved data offers an accurate and thorough reference.

Collectively, these studies highlight significant advancements in the identification, measurement, and modeling of catalyst and MEA degradation processes. These studies' comprehensive component-resolved insights provide a strong basis for creating and improving degradation-aware PEMWE systems, allowing for better predictive maintenance plans, increased operational robustness, and more efficient energy management procedures. In addition to membrane and catalyst deterioration, current research has concentrated on measuring and comprehending degradation events to enhance operational management and prediction accuracy of PEMWE systems.

An analysis conducted by Kimmel et al. [89] isolated and quantified voltage losses attributable to individual components of a commercial 250 cm2 PEMWE. At 0.5 A cm2, they found that replacing the catalyst-coated membrane (CCM) alone recovered more than two-thirds of the total performance losses. Subsequent refinements through polishing Ti-based porous transport layers (PTLs) and bipolar plates provided marginal additional improvements. This analysis underscores the dominant role of CCM aging, driven primarily by iridium agglomeration, ionomer redistribution, and trace calcium contamination, and provides experimentally-derived impedance parameters valuable for multi-physics aging models.

A long-term study was conducted by Tejera et al. [90] on a 25 cm2 Nafion 1110 CCM (3 mg Pt cm2 per side) to highlight the complexities associated with MEA degradation. After sequential potentiostatic (2 V at 60 °C) and galvanostatic (0.08 A cm^{-2}) tests spanning 168 h each, the study observed substantial increases in ohmic resistance (RΩ doubled) and significant charge-transfer resistance growth (threefold). There was a noticeable increase in mass-transfer resistance only above 2.3 V. The researchers demonstrated an effective mitigation strategy through a simple chemical rinse (1-h treatment in 1 M H_2SO_4 at 80 °C), restoring approximately 85 % of initial MEA performance and dramatically reducing the degradation rate from approximately 250 μA cm^{-2} h^{-1} to roughly 40 μA cm^{-2} h^{-1}. Consequently, early-stage performance loss is primarily caused by reversible cation contamination rather than irreversible structural deterioration. These findings provide actionable parameters for differentiating between recoverable fouling and irreversible degradation within predictive modeling frameworks.

Supporting these findings, Madhavan et al. [91] introduced a machine-learning-based corrosion model for coated PTLs. They trained extreme gradient boosting and artificial neural networks on corrosion current density and end-of-life voltage data, significantly accelerating prediction times compared to physics-based models. The best-performing model obtained a high level of predictive accuracy (R2 = 0.9393 for corrosion current density and R2 = 0.9666 for end-of-life voltage), highlighting the potential for data-driven approaches to quickly evaluate degradation risks resulting from specific PTL coatings.

Additional work by Lee et al. [92] provided a comprehensive quantitative understanding of membrane thinning due to radical attacks by integrating experimentally determined Fenton-rate constants into reaction-transport models. According to their study, material-specific degradation rates can vary significantly under operational conditions, indicating that porous-supported membranes have substantial potential to reduce cumulative thinning over prolonged periods of operation.

3.3. Degradation impact modeling

Given the increasing integration of RES into power systems, efficient power allocation and energy management have become paramount. RES, such as solar and wind power, are inherently intermittent and subject to fluctuating availability. This variability poses challenges to maintaining a stable power supply and managing energy generation. To ensure optimal utilization of RES and grid stability, effective power allocation strategies need to be implemented. It is possible to balance supply and demand, maximize system efficiency, and minimize curtailment by intelligently distributing and managing RES power. Furthermore, efficient energy management plays a crucial role in mitigating RES fluctuations' impacts on system components. It also reduces the degradation of power generation and conversion devices, such as PEMWE systems. By implementing advanced control and optimization techniques, it is possible to optimize energy flow, minimize degradation, and enhance the overall performance and longevity of PEMWE systems.

In their study Lu [83]. focuses on the optimization of power allocation in a wind-hydrogen system with a multi-stack PEMWE, considering degradation conditions. As illustrated in Fig. 5, degradation can have a significant impact on the efficiency of PEMWEs. The study contributes to slowing down degradation and improving the energy efficiency of multi-stack PEM water electrolyzer arrays in wind-hydrogen systems, providing practical significance for large-scale applications. They showed how researchers developed a three-dimensional multi-physics field model of PEMWE to analyze the relationship between efficiency and degradation. They proposed a power allocation strategy consisting of a control module and an execution module. The control module quantifies the electrolyzer degradation using the voltage degradation rate and determines power allocation to minimize degradation. The execution module utilizes an extended duty cycle interleaved buck converter controlled by fuzzy PID (Proportional-Integral-Derivative) control to supply power to each PEMWE stack. Computer simulations were conducted, and the results showed that the wind-hydrogen system achieved an energy efficiency of 61.65 % over one year of operation, with a voltage degradation of 7.5 V in the PEM water electrolyzer single-stack. The proposed power allocation strategy demonstrated efficient signal-following capability with low current ripple. Dynamic operation of PEMWE leads to degradation, resulting in increased operating voltage. PEMWE voltage degradation varies under different operating conditions, with frequent start-stop switching and high constant input power causing significant degradation, while low and medium constant input power has a lesser impact on degradation rates. Fig. 5 shows degradation-related increases in overpotential result in measurable efficiency losses across the entire input power range, confirming the importance of integrating degradation effects into system-level modeling and performance analysis.

With the assumption that voltage degradation rates under different operating conditions are independent of each other. In addition, all cells within the same PEMWE single stack exhibit the same performance. In accordance with this assumption, the total voltage degradation "ΔV_D" of the PEMWE single stack can be expressed in Eq. (16) based on ref. [83] as the cumulative effect of individual voltage degradation contributions

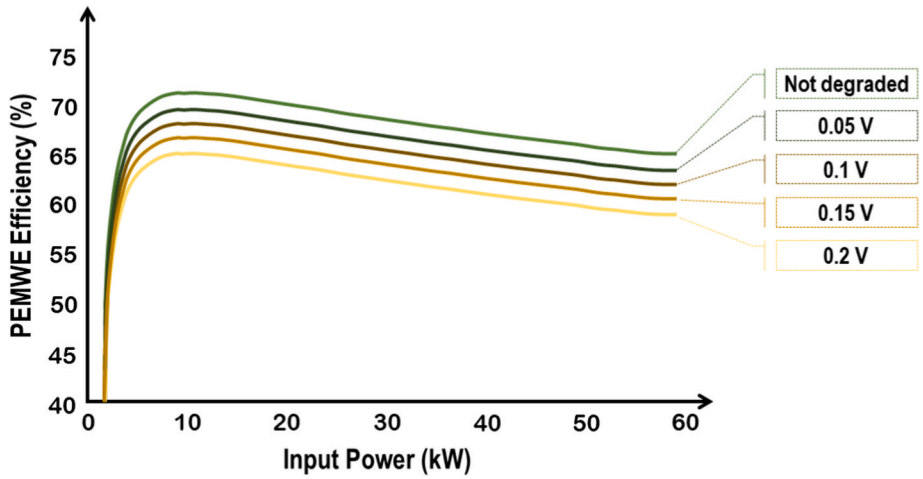

Fig. 5. Effect of different levels of degradation (expressed as overpotential increase) on PEMWE efficiency as a function of input power. The curves illustrate how degradation, modeled as an additional overpotential (0.05 V–0.2 V), progressively lowers the maximum efficiency and shifts the efficiency peak. This figure provides a clear visual representation of how degradation directly impacts system-level performance and efficiency, serving as a validation point for electrochemical degradation models [83].

from each cell.

$$\Delta V_D = n_{el} \times \left(V_{cr} \times t_{cr} + V_{ct} \times t_{ct} + V_{fh} \times t_{fh} + V_{fl} \times t_{fl} + V_m \times t_m\right) \quad (16)$$

The different operating conditions in Eq. (16) PEMWE system can be categorized as follows: "n_{el}" is considered as the number of electrolyzer's cells. "V_{cr}" stands for constant rated power operation, "V_{ct}" refers to constant turning power operation. Similarly, "V_{fh}" represents high power fluctuation operation, "V_{fl}" corresponds to low power fluctuation operation, and "V_m" denotes maintaining operation. These categories represent various modes of operation that can have distinct effects on the voltage performance of the system. In addition, the variable "t," with the same subscript as the voltages mentioned earlier, represents the duration or time that the PEMWE system operates in the corresponding operational mode. It serves as a parameter to indicate the length of time the system remains in a specific operational situation, such as constant rated power, constant turning power, high power fluctuation, low power fluctuation, or maintaining operation. The value of "t" influences the extent of voltage degradation experienced by the system during a particular operational mode.

Prediction of degradation is crucial for systems' long-term performance and durability. Various models and approaches have been developed to forecast degradation processes and estimate their impact on system operation. These predictive models for systems like PEMWE consider factors such as operating conditions, electrode materials, catalyst activity, water management strategies, and cell design. By analyzing degradation mechanisms, identifying key degradation indicators, and considering the interplay of multiple factors, these models provide valuable insights into degradation trends. They allow proactive maintenance and optimization strategies. By predicting degradation accurately in PEMWEs, energy management and power allocation can be improved, resulting in improved system efficiency and increased lifespan of the equipment. Furthermore, these predictive models aid in the development of advanced mitigation strategies, materials, and designs to minimize degradation effects. This will enhance PEMWE performance and reliability.

Degradation prediction in PEMWE under dynamic conditions can be achieved by considering the phenomenological dependence of current density on time. By accounting for the observed linearity of the High frequency resistance (HFR) over time, the authors derived an equation (Eq. (17)) that accurately describes the near-linear decrease of current density. The degradation rate of overpotential under galvanostatic conditions was also determined (Eq. (18)), showing a logarithmic increase with time and a slowing degradation rate. The projected average degradation rate over 100.000 h was approximately 0.6 μV/h. These findings emphasize the significance of minimizing both HFR and the rate of change of HFR ($d\Omega_{HF}/dt$) to mitigate degradation and achieve desired operational targets in PEMWEs.

$$i(t) = \frac{i(t_0) \times \Omega_{HF}(t_0)}{\left(\frac{d\Omega_{HF}}{dt}.t + \Omega_{HF}(t_0)\right)} \quad (17)$$

$$U_O(t) = \left(\frac{b}{2.303}\right).\log\left(\frac{d\Omega_{HF}(t)}{dt}.t + \Omega_{HF}(t_0)\right) + U_O(t_0) \quad (18)$$

In these equations "Ω_{HF}" stands for HFR ($\Omega.cm^2$), "t" is the desired time and "t_0" is the zero time (the existing situation for predictive purposes). "b" is part of the coefficients of the Tafel slope (it depends on materials and might change). "U_O" represents overpotential voltage in Volts [93].

4. Linking degradation phenomena to energy management and power allocation

The durability, efficiency, and performance of PEMWEs are critically influenced by degradation phenomena. The design of system architecture, alongside specific configurations and operational modes, plays a pivotal role in influencing the rates and patterns of degradation. Such variability necessitates careful consideration within the framework of energy management strategies and power allocation to optimize system performance and extend its lifespan. Understanding these factors is essential for developing robust PEMWE systems that can maintain high efficiency over time and adapt to varying operational demands.

This section provides a systematic review of existing literature that explores the role of degradation in the energy management and power allocation of PEMWEs. Initially, the review will highlight the importance of considering degradation in the energy management of PEMWEs, particularly electric vehicles and fuel cell/battery hybrids as discussed by Alyakhni et al. [94] and Wang et al. [95]. These studies emphasize the need for health-conscious energy management systems (EMSs) to extend vehicle lifespan and reduce running costs, incorporating both electrochemical and empirical models to mitigate the degradation of key components like Li-ion batteries and proton exchange membrane fuel cells (PEMFCs).

In addition to the static DMs, Dynamic Degradation Models (DDMs) capture the time-dependent behavior of PEMFCs, considering factors such as the start-stop cycle and load variations that affect the system

longevity. Multi-scale modeling approaches address different degradation mechanisms—from catalyst degradation to membrane deterioration—enabling targeted mitigation strategies [96–100].

Health management systems that integrate DMs are pivotal in extending the service life of PEMFCs by enabling real-time power allocation and proactive maintenance [101–106].

Operational strategies, considering load, temperature, and humidity, optimize energy usage and enhance the system's cost-effectiveness by mitigating degradation [107–124]. Fig. 6 illustrates the key considerations in the energy management of energy systems, encapsulating the interconnected roles of system design, degradation impact analysis, dynamic and multi-scale modeling, health management systems, and operational strategies. This graphical representation underscores the integrated approach required to effectively manage and mitigate degradation across different types of energy systems, ensuring optimal performance and extended system lifespan.

4.1. Degradation-mitigating operating strategies

Building upon insights into key considerations in energy management systems, this section identifies and prioritizes degradation modes specifically in the context of their implications for energy management and power allocation strategies within PEMWE systems. As opposed to revisiting the detailed mechanisms extensively discussed in Sections 2 and 3, the focus is placed here on establishing a direct connection between these degradation phenomena and practical energy management strategies.

Operational conditions such as current density and anode water content significantly affect the reliability of PEMWE systems, highlighting the necessity to incorporate these factors into energy management frameworks [68,125]. Adverse conditions, including high overpotential, elevated pressures, and suboptimal material selection, intensify degradation, especially affecting critical components like membranes, BPPs, and PTLs [63,126].

The intermittent nature of RES imposes dynamic operational conditions that exacerbate component degradation, as fluctuations disrupt stable power inputs, intensifying catalyst and membrane deterioration [127–130]. As a result of high input power levels, degradation is further accelerated, as there is an increase in thermal and mechanical stress, which, in turn, reduces the system's durability and efficiency [131]. Conversely, low power inputs can result in inadequate reactant supply and water management issues, reducing operational efficiency and potentially causing start-stop cycles, further amplifying mechanical stress [132–136].

As a result of start-stop cycling, thermal and mechanical stresses are inherently introduced, necessitating targeted operating strategies during shutdown periods to mitigate accelerated degradation [83,137]. During normal operation, gradual degradation through corrosion and impurities affects long-term performance, emphasizing the importance of comprehensive condition monitoring and predictive maintenance strategies [138–140]. Aging also naturally diminishes PEMWE system performance, emphasizing the need for integrated diagnostics, optimized control algorithms, and systematic maintenance to extend system life [141].

Understanding these operational degradation modes is essential to developing robust energy management and power allocation strategies, aiming at sustainable performance. As a reference point for further

Table 2
Classification of the effects of PEMWE operational degradation modes.

Degradation Mode	Result
High input power	Accelerate degradation due to increased stress Higher operating temperatures Dissolution of catalyst Agglomeration of catalyst Passivation of catalyst support Passivation of electrode Dissolution of membrane
Low input power	Insufficient power may lead to stop-start Reactant supply issues Decreased efficiency Poor local power distribution in cell
Input power fluctuations	Induce voltage fluctuations Temperature variations Poisoning of membrane Accelerating degradation mechanisms in CL, membranes, and electrodes
Start-stop cycles	Thermal and mechanical stress Material fatigue and degradation of catalysts and electrodes Agglomeration of catalyst Poisoning of membrane
Normal operation	Extended operation can result in gradual degradation catalysts, electrodes, and membranes due to chemical reactions, corrosion Impurity exposure
Pressure	Degradation in catalysts (poisoning) and electrodes
Temperature	Catalysts and electrodes membrane degradation
Ageing	Gradual catalyst loss, membrane deterioration Decline in electrode performance and Current reversal during power off Decreased efficiency and performance Catalyst poisoning

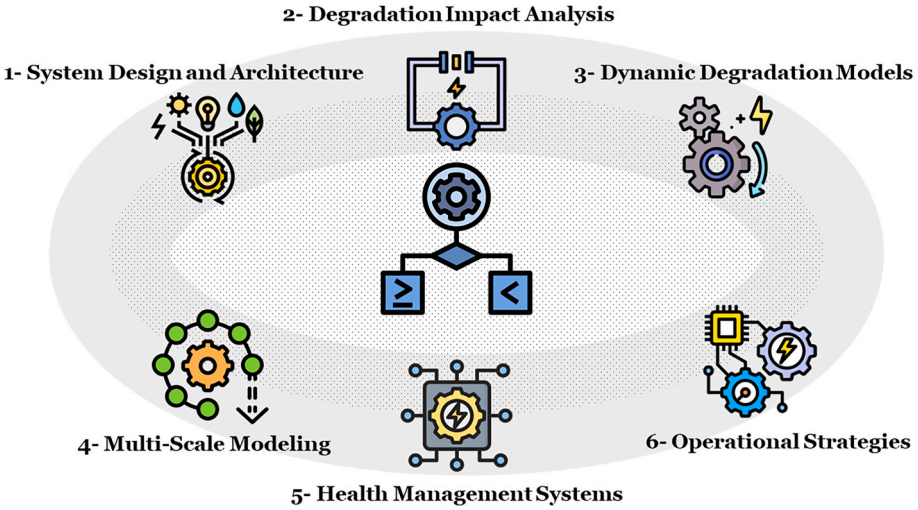

Fig. 6. Key considerations in energy management of energy systems.

optimization of PEMWE strategies, Table 2 provides a concise description of these operational degradation modes and their direct implications for PEMWE systems.

This understanding paves the way for developing robust control strategies and energy management schemes that address the specific degradation challenges associated with PEMWE systems. Understanding and effectively managing these degradation modes is crucial for optimizing the performance, efficiency, and durability of PEMWE systems. It enables the development of robust control strategies and energy management schemes tailored to address the specific degradation challenges associated with PEMWE systems. Fig. 7 illustrates the diverse operational conditions impacting PEMWE systems. It depicts various factors such as renewable energy inputs, power levels (high and low), power fluctuations, and operational modes like start-stop cycles. Also shown are environmental conditions like pressure and temperature, and system responses such as ageing, all contributing to the degradation dynamics of PEMWE systems.

Based on the literature review, Table 3 presents the reported and measured degradations in PEMWE systems under various operating modes. Degradation modes classification is crucial for understanding and managing performance degradation in PEMWE systems. The importance of this is particularly apparent when it comes to energy management and power allocation. Degradation modes include low or high input power, input power fluctuations, start-stop cycles, normal operation, pressure and temperature effects, and ageing. These degradation modes have significant implications for PEMWE systems' efficiency, durability, and overall performance, and understanding them is essential for effective mitigation strategies. By comprehensively examining these degradation modes, researchers and engineers can develop effective control strategies and energy management approaches to mitigate degradation. This will optimize system performance and extend PEMWE systems lifespan (see Table 4).

Table 3
PEMWE degradation in various working modes.

Mode	cell	Current density (A/cm^2)	T (h)	D	Unit	Ref.
System efficiency degradation	N/A	N/A	N/A	2.09	%/year	[142]
Under constant current	N/A	N/A	N/A	0–230	mV/h	[138]
Normal operation	50	2	8000	1.5	μV/h	[83]
Low power fluctuation operation	50	2	8000	50	μV/h	[83]
Constant turning power operation	50	2	8000	20	μV/h	[83]
High power fluctuation operation	50	2	8000	66	μV/h	[83]
Constant rated power operation	50	2	8000	196	μV/h	[83]
Solar fluctuating condition	N/A	1	N/A	3.5	mV/h	[133]
constant current condition	N/A	1	N/A	2.05	mV/h	[133]
fluctuating condition (average)	N/A	1	100	7.8	mV/h	[133]
Constant Current	1	N/A	7800	35.5	μV/h	[143]
Constant Current	9	N/A	4805	589	μV/h	[143]
continuously and a degradation rate	10	N/A	2000	1.5	μV/h	[144]
constant operation	1	2	N/A	194	μV/h	[145]
hydraulic cell compression constant current (65 °C)	1	2	600	4.43	μV/h	[140]
constant current	N/A	4	400	200+	μV/h	[47]
constant current	N/A	1	400	10 ± 30	μV/h	[47]
Dynamic	1	0.75	830	35.2	μV/h	[93] [137]

4.2. Integrating degradation models into energy management

Integrating degradation models into EMSs is essential for optimizing PEMWE operations, particularly in modular multi-stack configurations. Among the recommendations made by Sayed-Ahmed et al. is that optimizing operational parameters can significantly reduce the adverse effects of load fluctuations and frequent on/off cycling on system durability and efficiency [146].

Traditional energy management approaches, such as equal current distribution among stacks, have been challenged for causing suboptimal performance and accelerated degradation under persistent low-load conditions [147]. In contrast, sequential power allocation methods are more efficient, however, they may result in uneven degradation due to the concentrated use of certain stacks [148]. Advanced adaptive strategies presented by Guilbert and Vitale [149] and Han et al. [148] have dynamically adjusted power allocation based on real-time performance metrics, demonstrating efficiency improvements ranging from 5 % to 10 % compared to conventional methods.

Luxa et al. [150] introduced a multilinear time-invariant framework that automatically appends detailed stack, degradation and controller sub-models into a 100-stack PEM electrolyzer plant model. One-year

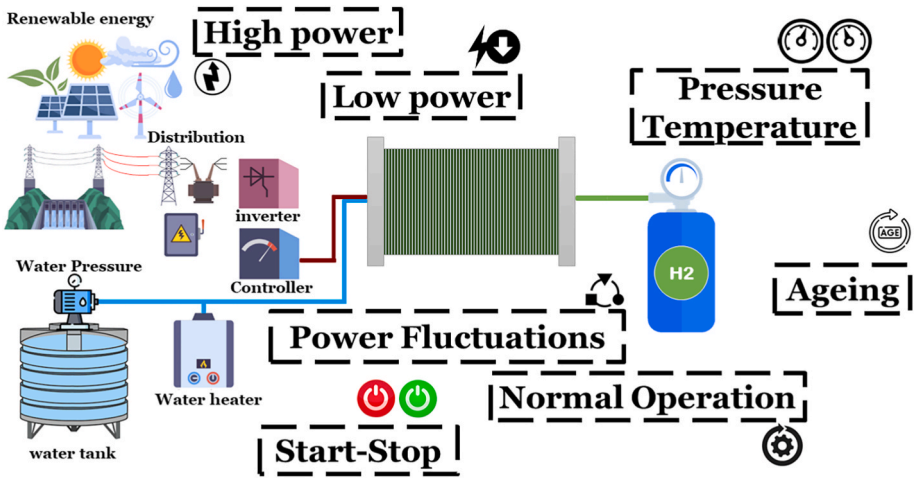

Fig. 7. Operational dynamics and degradation influences in PEMWE systems.

Table 4
Some PEMWE degradation prevention strategies that involve power allocation and energy management.

Focus	Mitigation strategy	Method	Result	Ref.
Thermal stress	Parametric optimization and control	Predictive Controller	Successful temperature control	[161]
Power allocation	Optimization	Extended duty cycle interleaved buck converter	slows down the degradation/improves the system energy efficiency	[83]
High Frequency resistance	Prediction	Identifying the location of high corrosion inhibiting or long-lived species	recoverable stationary deactivation	[93]

simulations driven by 10-min wind data revealed that an equal-current dispatcher achieved a higher mean stack efficiency (86.8 %) but also a slightly larger annual degradation gain (9.61 %) than a maximum-load strategy (82.3 % efficiency, 9.35 % degradation). The study demonstrates how explicitly embedding degradation states in the supervisory controller makes it possible to quantify and optimize the lifetime-versus-efficiency compromise, while the multilinear time-invariant representation keeps the computational cost low enough to run year-long scenarios on a desktop PC.

A number of heuristic and optimization-based frameworks have also been developed. To decrease transient-related wear, Lu et al. [71] devised an adaptive scheduling strategy employing fuzzy logic and local control indications, while Tully et al. [151] suggested a flexible load-sharing scheme based on stack-specific degradation sensitivity. A cost-weighted, degradation-aware model predictive control algorithm was introduced by Hong et al. [20], which dynamically reassigns power in response to real-time degradation forecasts. Cheng et al. [152] advanced this by integrating component-specific aging rates into a hierarchical EMS, balancing system-wide hydrogen production efficiency against predicted stack longevity. These approaches highlight the value of hybrid strategies that combine empirical degradation data with optimization theory to enable robust, lifetime-aware dispatch.

There has been a significant shift in recent years from simplistic loading methods based on rules to more sophisticated approaches based on optimization. Mixed-integer linear programming (MILP) models are employed to schedule stack on/off states hourly, explicitly accounting for degradation-related penalties, startup costs, and electricity pricing signals [153]. Rolling-horizon model predictive control (MPC), which continually modifies set-points in response to changes in renewable energy estimates, improves dispatch efficiency at the minute level [154].

Parallel advancements integrate explicit degradation terms directly into optimization objectives. Similarly, Zheng et al. [155] used membrane voltage-rise per coulomb as part of their optimization objective to coordinate operational power towards stacks that lie along the optimal-efficiency frontier while simultaneously minimizing cumulative degradation. Similarly, heuristic methods such as FIFO rotation and segmented fuzzy logic approaches effectively reduce daily start-stop cycles by more than 40 % compared to fixed-priority methods and deliver higher hydrogen yields [20,156,157]. A dedicated PEMWE study using deep-learning degradation prediction has just been reported by Xu et al. [158]. By training a CNN-LSTM network on 1140 h constant-load and 660 h start-stop durability datasets, the authors forecast cell-voltage drift 1000 h ahead with $\leq$5 mV absolute error ($R^2 \approx 0.98$) and demonstrate that start-stop operation halves the degradation rate compared with steady current. Their data-driven framework therefore offers a practical route to real-time, state-aware degradation models suitable for integration into supervisory EMS algorithms.

Multi-agent systems, exemplified by Henkel et al. [159], leverage module-type-package standards, employing distributed optimization methods such as the Alternating Direction Method of Multipliers (ADMM). In addition to maintaining near-optimal performance comparable to centralized MILP strategies, this approach improves fault tolerance and scalability, making it feasible to implement plug-and-play solutions.

Despite these advances, current methodologies often depend heavily on simplified or heuristic degradation models, limiting predictive accuracy and applicability in industrial environments [20,64]. In recognition of these limitations, recent research emphasizes the importance of incorporating detailed, experimentally validated degradation models to increase predictive accuracy and practical applicability.

Endrődi et al. [160] demonstrated through real-world field data and scenario modeling that operating mode selections, such as transitioning from photovoltaic-only to grid-assisted baseload operation, significantly impact both hydrogen production costs and degradation rates. It is apparent from recent research that the importance of incorporating detailed, experimentally validated degradation models is paramount in enhancing predictive reliability and practical applicability.

Further practical integration was shown by Ogumerem and Pistikopoulos [161], who embedded detailed thermal degradation constraints directly into an explicit MPC framework. As a result, real-time thermal management has been enabled, which has proved crucial to extending the life of PEMWE by maintaining membrane temperature variations within strict operational limits.

Additionally, Javed et al. [162] introduced state-aware degradation modeling, clustering over 4000 operational hours into distinct operational states (quasi-steady, ramp-up, and idle), and quantified specific voltage-decay rates for each state. The lifetime-average energy efficiency was greatly increased by using state-dependent degradation coefficients in predictive EMS, which also reduced degradation-related energy penalties to about 13 %.

The ongoing evolution towards embedding sophisticated degradation models into operational decision-making underscores the industry's trajectory toward adaptive, precise, and robust PEMWE management solutions. Therefore, future approaches should balance computational efficiency with the accuracy of degradation predictions, allowing real-time application in industrial environments.

5. Future trends

To maximize the benefits and further the advancement of PEMWE technology, it is essential to identify and outline crucial future directions based on a comprehensive literature analysis. This chapter discusses key future trends and areas for further investigation that are critical to the advancement of PEMWE degradation research. As well as highlighting crucial steps for future research, this chapter emphasizes the essential need for ongoing innovations and explorations in the field of PEMWE degradation and energy management. These recommendations act as a blueprint for focused studies, aiming to refine and optimize the efficiency and reliability of HyPro systems through innovative degradation management and energy solutions. Fig. 8 illustrates the key areas of technological innovation and degradation management that are essential to improving the sustainability and environmental impact of PEMWE. It emphasizes the integration of renewable energy sources with predictive degradation models and advanced diagnostic tools, highlighting future directions for enhancing system durability and energy efficiency in green hydrogen production.

Key Focus Areas for Future Research:

Standardization: Essential for consistent evaluation and benchmarking, standardization ensures uniformity in testing protocols and

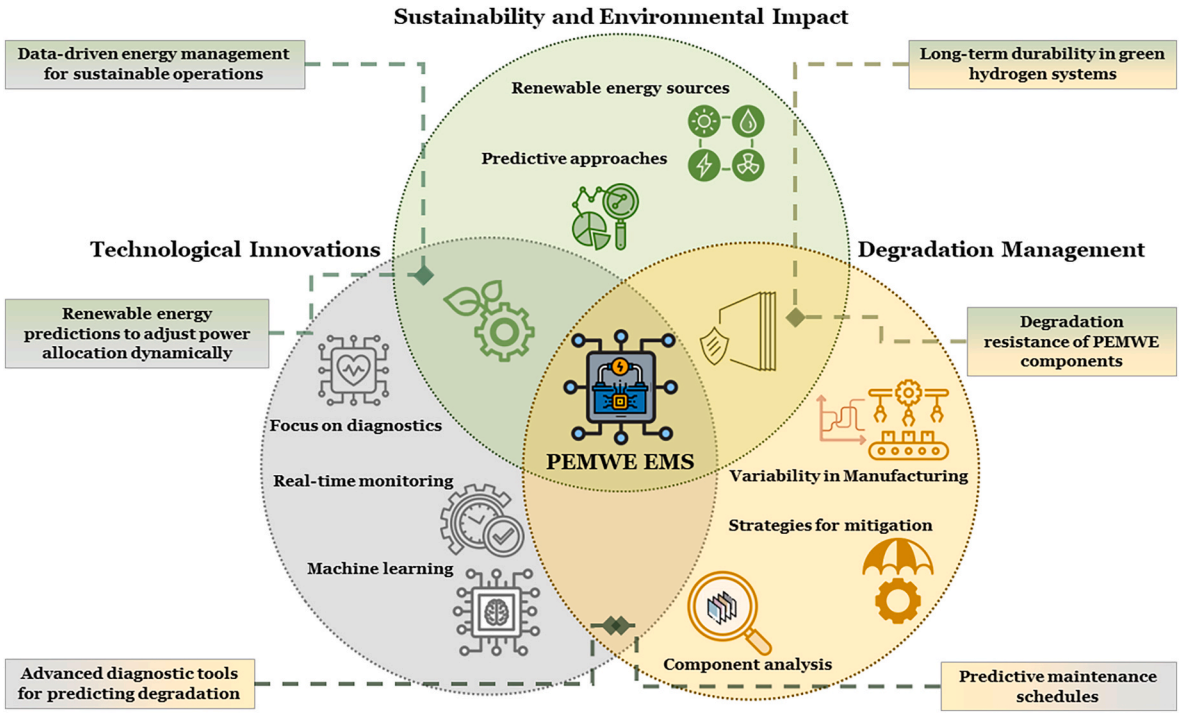

Fig. 8. Integration of technological innovations and degradation management in PEMWE systems for enhanced sustainability.

degradation rate measurements across different studies. This facilitates comparative analysis and fosters advancements in PEMWE technology. Tomic et al. [24] underscore the need for standardized degradation tests and proper activation procedures to ensure accurate evaluations of PEMWE durability.

Utilizing Existing FC Formulas: Adapting generalized formulas from fuel cells (FC) to fit the specific needs of electrolyzers can significantly enhance the prediction and mitigation of degradation in PEMWE systems. This approach promotes a systematic analysis of degradation mechanisms and assists in optimizing PEMWE performance and longevity.

Manufacturing Variability and Component Differences: Acknowledging the diversity in PEMWE components and manufacturing techniques is crucial for accurate degradation analysis. Tailoring studies to account for these variations ensures a deeper understanding of how different factors contribute to system degradation.

Degradation Measurement Across Operating Modes: It is critical to measure degradation under various operating conditions to fully understand how different modes impact system performance. Future research should focus on integrating comprehensive measurement techniques to develop robust maintenance strategies and optimize operational guidelines.

Green HyPro: With the integration of RESs such as solar and wind, understanding the degradation mechanisms specific to PEMWE systems used for green HyPro is imperative. Future studies should explore long-term performance and standardized testing protocols to enhance system efficiency and sustainability.

Prevention of Degradation: Prioritizing the prevention of degradation through improved fabrication techniques, optimized operating conditions, and predictive maintenance strategies is essential for enhancing the durability and cost-effectiveness of PEMWE systems. Shakhshir et al. [163] discuss the impact of clamping methods on current distribution in PEMWE cells, highlighting the need for careful selection of assembly techniques to ensure optimal performance.

Advancements and innovations:

Technological Innovations: Future trends may include the development of advanced diagnostic tools and real-time monitoring systems, utilizing machine learning algorithms to predict and mitigate degradation actively.

Material and Catalyst Development: Developing new materials and catalysts can result in significant improvements to the structural integrity and efficiency of PEMWE systems.

Energy Management and Power Allocation: Optimizing power allocation strategies for green hydrogen systems and incorporating advanced data analysis techniques could greatly enhance the operational efficiency and lifespan of PEMWE systems.

Sustainable Practices: Emphasizing sustainability, future research should also focus on reducing the environmental impact of HyPro and enhancing the integration of PEMWE systems with RESs.

For future studies, it is highly recommended to focus on advancing fabrication techniques, exploring novel materials and catalysts, developing real-time monitoring and control systems, and implementing machine learning algorithms for predictive maintenance and optimization. These efforts will contribute to the development of more efficient, reliable, and durable PEMWE systems, accelerating the transition towards sustainable and clean energy technologies.

6. Conclusions

This review emphasizes the critical impact of degradation phenomena on PEMWE operational sustainability and efficiency. An improved EMS and power allocation framework can enhance system efficiency and lifespan by incorporating detailed degradation phenomena. The insights derived from robust, experimentally validated degradation models not only enhance real-time operational decision-making but also provide essential parameters for predictive maintenance and system optimization. Such integration is critical as the global transition towards renewable energy necessitates reliable and economically sustainable hydrogen production.

To maximize PEMWE efficiency, reliability, and operational lifespan, precise degradation modeling and predictive management techniques become essential drivers. According to the paper, robust and sophisticated degradation modeling strategies, validated using empirical data, can significantly mitigate performance loss and enhance the durability

of PEMWE components. PEMWE systems should be designed to achieve improved operational sustainability and economic viability by utilizing advanced computational techniques and novel materials in future research.

Future research and technological development should continue prioritizing the refinement of degradation models, exploring innovative materials and fabrication methods, and embedding advanced diagnostic and predictive techniques into real-time operational control systems. By addressing the computational complexity of these approaches, a balance can be achieved between predictive accuracy and practical applicability in industrial environments. It is estimated that implementing these integrated strategies will contribute to the broader adoption and scalability of PEMWE technology, contributing to the goal of global decarbonization and sustainable energy production.

CRediT authorship contribution statement

Ashkan Makhsoos: Writing – original draft, Visualization, Methodology, Conceptualization. **Mohsen Kandidayeni:** Writing – review & editing, Validation, Supervision. **Bruno G. Pollet:** Writing – review & editing, Supervision. **Loïc Boulon:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

Data availability statement

No external data were used for the research described in this article; all relevant information is included within the article itself.

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.

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Nomenclature:

$\mathbf{V}_{\mathrm{Hcal}}$	HyPro calculated volume
$\mathbf{V}_{\mathrm{HyPro}}$	HyPro actual volume
$\mathbf{E}_{\mathrm{HyPro}}$	Productive energy
$\mathbf{E}_{\mathrm{input}}$	Input energy
$\mathbf{P}_{\mathrm{el}}$	electrolyzer required power
$\mathbf{R_f}$	Fluor release (mol/s)
$\mathbf{T_r}$	operating reference temperature (°C)
$\mathbf{U_a}$	Activation overvoltage (v)
$\mathbf{U_c}$	Concentration overvoltage (v)
$\mathbf{U_o}$	Ohmic overvoltage (v)
$\mathbf{V_C}$	cell voltage (v)
$\mathbf{V_M}$	Molar volune
$\mathbf{V_O}$	reversible (open circuit) voltage (v)
$\mathbf{V_S}$	stack voltage (v)
$\mathbf{V}_{\mathrm{cell}}$	cell voltage (v)
$\mathbf{V}_{\mathrm{cn}}$	each cell voltage (v)
$\mathbf{V}_{\mathrm{ct}}$	Constant turning power operation voltage degradation
$\mathbf{V}_{\mathrm{fh}}$	High power fluctuation operation voltage degradation
$\mathbf{V}_{\mathrm{fl}}$	Low power fluctuation operation voltage degradation
$\mathbf{V_m}$	maintaining operation voltage degradation
$\mathbf{V}_{\mathrm{rev}}$	reversible cell voltage (v)
$\mathbf{V}_{\mathrm{th}}$	thermoneutral voltage (v)
$\boldsymbol{n_e}$	Number of electrons
$\mathbf{n}_{\mathrm{el}}$	number of electrolyzers
$\mathbf{t_r}$	reference time
$\Delta\mathbf{V_D}$	Total voltage degradation
$\mathbf{\Omega}_{\mathrm{HF}}$	High frequency resistance ($\Omega.\mathrm{cm}^2$)
$\boldsymbol{\delta}_{\mathrm{DR}}$	Conductivity loss degradation rate
$\boldsymbol{\delta_M}$	Membrane thickness
$\boldsymbol{\eta_F}$	Faradaic efficiency (%)
$\boldsymbol{\eta}_{\mathrm{PS}}$	PEMWE System efficiency (%)
$\boldsymbol{\eta}_{\mathrm{au}}$	Auxiliary equipment efficiency (%)
$\boldsymbol{\eta_c}$	cell efficiency (%)
$\boldsymbol{\eta_e}$	Electrolyzer efficiency (%)
$\boldsymbol{\eta_s}$	System efficiency (%)
$\boldsymbol{\lambda}_{\mathrm{age}}$	Conductivity loss degradation
$\boldsymbol{\lambda_0}$	Conductivity loss degradation in zero time
A	Area (square meter, m^2)
D	Degradation (μV/h)
E	Energy ($Wh \approx 3600\, joules$)
F	Faraday's constant
F	Faraday constant (C/mol)
g	gradient
P	Power (W)
t	Time (h and H/2)
t	Time (h)
W	electrical work of electrolysis (J/mol)
$\mathrm{W}_{\mathrm{irrev}}$	Irreversible energy (J/mol)
$\mathrm{W}_{\mathrm{rev}}$	Reversible energy (J/mol)

(*continued on next page*)

(*continued*)

Υ	surface coverage ratio (/)
$\Delta\delta_M$	Thinning of membrane thickness
ΔH_R^0	Electrolysis required energy (J/mol)
ΔT	Operating time (h)

Abbreviations:

BoL	Beginning of Life
BPP	Bipolar Plate
CL	Catalyst layer
DM	Degradation model
e-	electron
EM	Energy management
EMS	Energy management system
FC	Fuel Cell
GDL	Gas Diffusion Layer
H_+	Protons (isolated hydrogen ions)
H_2	Hydrogen
H_2O	Water
HFR	High Frequency Resistance
HHV	Higher Heating Value
HyPro	Hydrogen Production
L	Liter
LHV	Lower Heating Value
MEA	Membrane Electrode Assembly
O_2	Oxygen
OER	Oxygen Evolution Reaction
PEM	Proton Exchange Membrane
PEMFC	Proton Exchange Membrane Fuel Cell
PEMWE	Proton Exchange Membrane Water Electrolyzer
PSL	porous sintered layer
PTL	porous transport layer
RES	Renewable Energy Source
AST	Accelerated Stress Testing

Data availability

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

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