Highlights

Toward optimal operations of long-lifetime PEM electrolysis: degradation mechanisms, modeling, diagnostics, and control

Islam Zerrougui, Zhongliang Li, Daniel Hissel

- Discuss systematically on degradation mechanisms, modeling, diagnostics and control.
- Clarify the interactions among the elements involved in PEMWE system operation.
- Propose an integrated optimization framework to achieve optimal operation.
- Provide prospects on various aspects toward the PEMWE optimal operation.

Toward optimal operations of long-lifetime PEM electrolysis: degradation mechanisms, modeling, diagnostics, and control

Islam Zerrougui[a], Zhongliang Li[a,*] and Daniel Hissel[a,b]

[a] *Université Marie et Louis Pasteur, UTBM, CNRS, Institut FEMTO-ST, FCLAB, F-90000 Belfort, France*
[b] *Institut Universitaire de France (IUF), Paris, France*

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ABSTRACT

The global shift towards sustainable energy technologies has underscored the importance of efficient hydrogen production methods. Polymer Electrolyte Membrane Water Electrolysis (PEMWE) has emerged as a possible solution due to its high efficiency, rapid response capabilities, and seamless integration with renewable energy sources such as solar and wind power. Optimizing PEMWE operations is crucial for enhancing performance metrics including efficiency, durability, reliability, and cost-effectiveness. This paper presents a comprehensive literature review focusing on the key elements necessary for optimizing PEMWE operations facing a variety of degradation mechanisms and encompassing advanced modeling techniques, diagnostic tools, and control strategies. Various modeling approaches are explored, from static lump-parameter to dynamic and multi-dimensional ones, highlighting their roles in capturing the complex multi-physics phenomena inherent in PEM systems. Diagnostic methods, from electrochemical and physical to software-based ones, are examined for their effectiveness in identifying and mitigating degradation mechanisms that compromise system longevity and performance. Additionally, state-of-the-art control strategies are discussed, focusing on regulating critical operational parameters such as current density, temperature, water flow, and pressure, thereby maintaining optimal operating conditions. By integrating insights from multiple disciplines, this review proposes an Integrated Optimization Framework that serves as a roadmap for advancing PEMWE technology toward its optimal potential. The framework addresses current challenges and identifies future research directions aimed at enhancing the efficiency, durability, and overall performance of PEM electrolysis, thereby contributing to the realization of a sustainable hydrogen economy.

1. Introduction

The global energy landscape is undergoing a significant transformation toward sustainable and clean alternatives to mitigate climate change and reduce greenhouse gas emissions. Among emerging energy carriers, hydrogen has gained prominence due to its potential as a clean, efficient, and versatile fuel. Hydrogen can serve as a viable substitute for traditional fossil fuels in various forms-gaseous, liquid, or solid offering pathways to decarbonize multiple sectors including transportation, industry, and power generation [1]. Despite being the most abundant element in the universe, hydrogen is relatively scarce in its free form on Earth, necessitating efficient production methods from both fossil fuels and renewable energy sources [2, 3]. Around 78% of global hydrogen production relies on fossil fuel reforming, 18% on coal gasification, and about 4% is produced through electrolysis [4]. While fossil fuel-based technologies dominate large-scale hydrogen production due to their efficiency and established infrastructure, they generate substantial carbon dioxide emissions, undermining environmental sustainability efforts [5]. In contrast, hydrogen produced via water electrolysis, especially when powered by renewable energy sources, offers a highly pure form without direct carbon emissions, making it an environmentally advantageous alternative. Consequently, electrolysis-based hydrogen production is expected to experience considerable growth in the future [5].

Water electrolysis involves splitting water molecules into oxygen (O_2) and hydrogen (H_2) through the application of electrical energy [6]. An electrolysis cell comprises two main compartments: the anode, where oxidation occurs generating oxygen gas, and the cathode, where reduction occurs producing hydrogen gas. Various water electrolysis technologies exist, categorized by system architecture, operating temperature levels, and electrolyte type. The most prominent methods include Alkaline Water Electrolysis (AWE), Solid Oxide Electrolysis (SOE), Anion Exchange Membrane Electrolysis (AEM), and Proton Exchange Membrane Electrolysis (PEM). Among these, PEM water

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[*] Corresponding author: Zhongliang Li. Email: zhongliang.li@univ-fcomte.fr
ORCID(s):

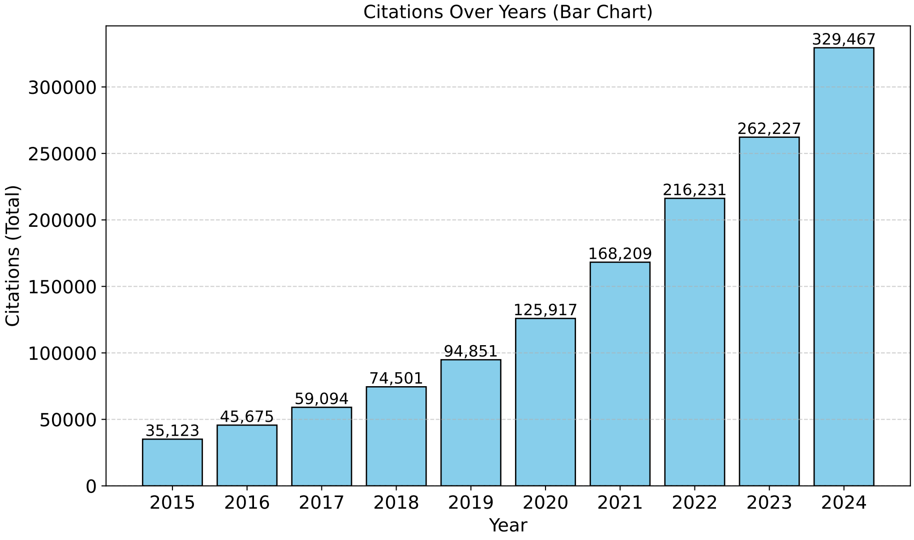


Figure 1: Total Citations per year for PEM Electrolysis System (2015-2024), data obtained from App.Dimensions

electrolysis (PEMWE) stands out due to its compact system design, high current density capabilities, high cell voltage efficiency, elevated operational pressures, and rapid response times [7]. Reflecting this growing interest, citations for PEM electrolysis have increased from 35,123 in 2015 to 329,467 in 2024, as illustrated in Fig. 1 (data obtained from App.Dimensions). Despite its advantages, several challenges hinder the widespread adoption of PEM electrolysis, including high material costs, performance degradation over time, and the need for advanced control strategies to optimize operation and integrate with renewable energy systems [8]. Achieving high water electrolysis efficiency while minimizing material costs remains a primary challenge. In this work, three criteria are used to describe the electrolysis's performance: efficiency, durability, and overall system performance.

- Efficiency in PEM water electrolysis refers to the system's ability to convert electrical energy into chemical energy stored in hydrogen with minimal losses. High efficiency implies large amount of hydrogen being produced per unit of energy consumed, reducing operational costs and improving sustainability.
- Durability pertains to PEM electrolysis's longevity and consistent performance over time, affected by material degradation and operational conditions.
- Overall system performance encompasses not only efficiency and durability but also factors such as operational flexibility, response time, safety, and ease of integration with renewable energy systems.

Achieving optimal performance in PEM electrolysis systems requires a systematic enhancement of these operational criteria through several interrelated tasks, including the investigation of degradation mechanisms, modeling, diagnostics, and control design.

Optimizing electrolysis operation necessitates a comprehensive understanding of various mechanisms that impact the performance, especially those affecting the durability. Mitigating the degradation effects is essential for extending the electrolysis's lifespan. However, identifying degradation pathways is particularly challenging due to their interconnected nature within the cell. This complexity necessitates advanced diagnostic tools capable of pinpointing different forms of degradation, determining their root causes, and evaluating their consequences. Such insights are foundational for mitigating degradation by optimizing operational parameters and selecting appropriate materials and control laws.

Developing robust models that accurately capture the coupled complex phenomena within PEM electrolysis, including fluid dynamics, electrochemistry, mass transport, thermal management, and material degradation, is crucial. Modeling serves as a powerful tool to represent the system through mathematical equations, facilitating a deeper understanding of underlying physics and providing predictive insights. However, modeling PEM electrolysis is challenging due to the diverse physical processes involved, such as fluidic, electrical, and thermal subsystems, along with two-phase flows of gas bubbles and liquid water. These processes exhibit multiphysics, multiscale, and nonlinear characteristics, complicating model identification and validation. Additionally, intricate geometries and the micromorphologies of system components add further complexity to the model parametrization.

Furthermore, applying advanced control strategies emerges as a pivotal approach to enhance efficiency and extend the PEMWE lifetime. Selecting appropriate control objectives and parameters is essential for achieving optimal operating conditions. Implementing adaptive controllers allows for real-time adjustments to operational conditions, balancing system efficiency with degradation rates to maximize overall performance. Control strategies must consider the dynamic behavior of the PEMWE, including transient responses to fluctuating input power when integrated with renewable energy sources. Moreover, the control should also be conducted in consideration of the performance degradation status and aimed at mitigating the degradation evolution.

Beyond fundamental research, recent works emphasize that optimal PEMWE operation must explicitly incorporate lifetime-aware considerations. Schofield et al. [9] developed a dynamic optimization framework linking operational scheduling with degradation models, highlighting the need to trade off short-term efficiency against long-term durability. Similarly, Liu et al. [10] reviewed recent advances in PEMWE optimization strategies and pointed to the integration of degradation-aware control as a major research gap.

The Integrated Optimization Framework presented in Fig. 2 serves as a cornerstone of this review, encapsulating the interplay between degradation mechanisms, modeling, diagnostics, and control strategies within PEM electrolysis systems. This holistic framework addresses the multifaceted challenges of optimizing the efficiency, durability, and overall performance of the PEM electrolysis. At its core, the Modeling Module integrates detailed representations of the PEM electrolysis process, synthesizing data from degradation mechanism investigations to provide predictive insights into pathways that impact system longevity and performance. Surrounding the modeling core, the Diagnostics and Control components form a feedback loop essential for real-time system optimization. Diagnostic information feeds into the modeling module, enabling continuous updates and refinements to the predictive models, ensuring responsiveness to actual operating conditions and degradation trends. The Control Strategies module utilizes insights from both modeling and diagnostics to implement proactive adjustments to operational parameters. By employing advanced control techniques such as adaptive controllers and observer-based systems, the framework mitigates the effects of degradation, optimizes hydrogen production efficiency, and extends the PEMWE lifespan. This integration ensures that the system operates under optimal conditions, balancing performance gains with durability considerations.

In essence, the Integrated Optimization Framework offers a structured approach to tackling the complexities of PEM electrolysis. By interlinking degradation investigations, modeling, real-time diagnostics, and intelligent control, the framework not only addresses current challenges but also paves the way for future advancements in PEM electrolysis technology. This integrated approach is pivotal for achieving high operational efficiency and long-term durability, thereby enhancing the viability of hydrogen as a sustainable energy carrier.

This review highlights and discusses recent approaches to optimization in PEM electrolysis. It introduces an Integrated Optimization Framework as a new conceptual roadmap that encapsulates the interplay among degradation mechanisms, modeling, diagnostics, and control. This framework serves as a unifying paradigm for improving long-term efficiency and durability, linking insights from multiple disciplines into a single integrated strategy. The review further synthesizes a wide range of literature - from materials degradation and advanced modeling techniques to diagnostic tools and control design - into a coherent perspective on optimal PEMWE operation. Unlike existing surveys, which often emphasize only one aspect, such as material durability or specific operating regimes, this work provides a comprehensive outlook that highlights the interdependencies of all critical factors. Together, these contributions establish a holistic roadmap for long-lifetime operation and offer valuable guidance for future research and technology development.

The remainder of the paper is organized as follows: First, the fundamental components of PEM electrolysis are described, emphasizing the importance and recent progress in key materials. Next, various modeling approaches for each subsystem are detailed, ranging from zero-dimensional to multi-dimensional models. Advanced diagnostic techniques for PEM electrolysis are then presented, followed by a summary of current degradation mechanisms affecting different cell components. Subsequently, the paper explores existing control strategies for various subsystems, aiming to optimize operational conditions and improve overall efficiency. A dedicated section on future prospects is then presented, and the paper concludes with final remarks.

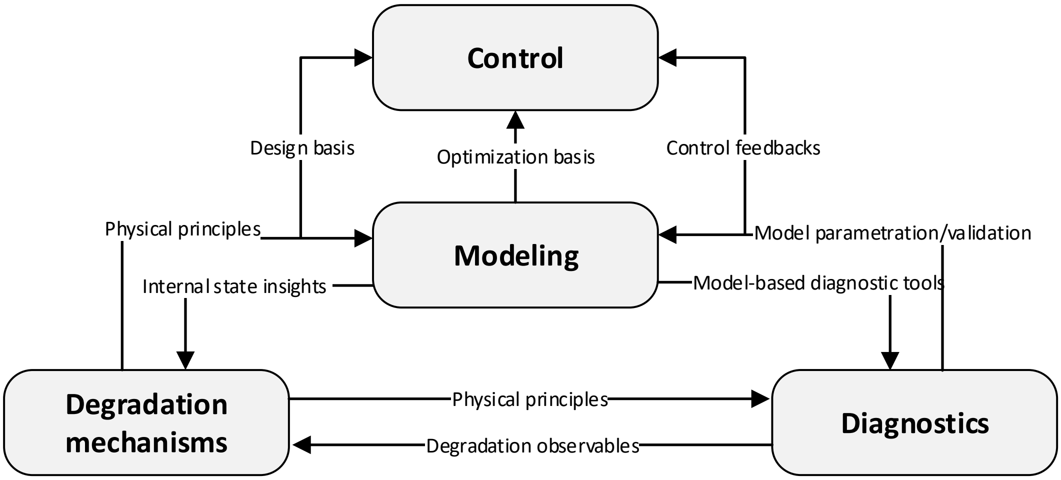


Figure 2: Integrated operation optimization framework for PEM electrolysis

2. PEM electrolysis principle: from material to system

PEM electrolysis is a complex system that depend on the integration of various components to efficiently split water into hydrogen and oxygen. Understanding the roles, material requirements, and recent advancements of these components is essential for optimizing the performance, efficiency, and durability of PEM electrolysis systems.

2.1. Components

A typical electrolysis cell comprises a Membrane Electrode Assembly (MEA), Porous Transport Layers (PTLs), and Bipolar Plates (BPs). These components are assembled in a layered structure, as depicted in Fig. 3

2.1.1. Membrane Electrode Assembly

MEA is central to the operation of a PEM electrolysis. It consists of a proton-conducting membrane sandwiched between two catalyst layers. The membrane serves two critical functions: conducting protons (H^+) from the anode to the cathode and acting as a physical barrier to prevent the mixing of hydrogen and oxygen gases produced at the respective electrodes. Perfluorosulfonic acid (PFSA) polymers, such as Nafion, Flemion, or Aquivion, are commonly used as membrane materials due to their excellent proton conductivity, chemical stability, and mechanical strength [11]. High proton conductivity minimizes ohmic losses, enhancing overall cell efficiency. The membrane must also exhibit low gas permeability to prevent gas crossover, which can reduce product purity and pose safety risks. Membrane thickness (50–200 μm) is a crucial parameter influencing performance and durability. Thinner membranes reduce ohmic resistance, improving efficiency [12]. However, excessively thin membranes may lead to increased gas crossover and reduced mechanical integrity [8]. Therefore, optimizing membrane thickness involves balancing proton conductivity, gas impermeability, and mechanical robustness. Despite their advantages, PFSA membranes are expensive due to the complex manufacturing processes and high material costs. Moreover, they were initially developed for fuel cells and may not be fully optimized for PEMWE conditions [13]. Consequently, research efforts are focused on developing alternative membranes that are cost-effective and tailored specifically for PEM electrolysis. One approach involves the development of hydrocarbon-based membranes, which offer potential cost advantages and reduced gas crossover compared to PFSA membranes [14]. However, these membranes may exhibit lower chemical stability and durability under the harsh oxidative conditions of the PEMWE. Another strategy is the use of composite membranes that incorporate inorganic fillers or reinforcement materials to enhance mechanical strength, and proton conductivity, and reduce gas permeability [8].

The catalyst layers play a crucial role in facilitating the electrochemical reactions at the anode and cathode. They are typically composed of catalyst nanoparticles dispersed within an ion-conducting binder (see Fig.3), forming a porous structure that facilitates the transport of reactants and products. At the anode, the catalyst facilitates the Oxygen Evolution Reaction (OER), where water molecules are oxidized to produce oxygen gas, protons, and electrons. The OER is kinetically sluggish and requires a high overpotential, making it a major bottleneck in achieving high efficiency

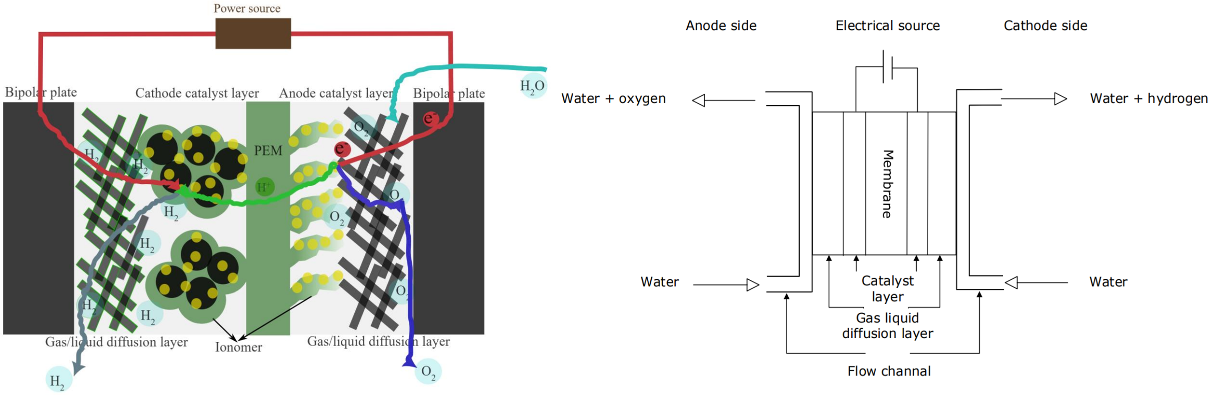


Figure 3: Schematic diagram of classic PEM electrolysis cell components

[15]. Currently, iridium-based catalysts, such as iridium oxide (IrO_2), are considered the most effective for the OER in PEM electrolysis due to their excellent activity and stability in acidic and oxidative environments [16]. However, the scarcity and high cost of iridium significantly contribute to the overall cost of the PEMWE [17]. To address these challenges, research is focused on reducing iridium loading by developing nanostructured catalysts with high surface areas [18]. Alternative catalysts, such as ruthenium oxides and mixed metal oxides, are also being explored. Additionally, using conductive and corrosion-resistant support materials, like titanium oxides, can enhance catalyst dispersion and durability [19]. At the cathode, the catalyst facilitates the Hydrogen Evolution Reaction (HER), where protons combine with electrons to form hydrogen gas. The HER is a relatively faster reaction with lower overpotential requirements. Platinum (Pt) is the preferred catalyst due to its high electrocatalytic activity and stability in acidic environments [16]. However, the high cost of platinum drives research toward reducing Pt loading and developing non-precious metal catalysts, such as transition metal phosphides or sulfides, to lower costs while maintaining performance. Innovations in catalyst design, including core-shell nanoparticles, alloys, and single-atom catalysts, are being pursued to enhance activity and reduce precious metal usage [8]. These advancements aim to develop cost-effective and efficient catalyst layers that contribute to the overall optimization of PEM electrolysis [20]. Recent studies emphasize that not only the catalyst itself but also the membrane-electrode interactions are critical: uneven ionomer distribution within the catalyst layer can increase mass transport resistances and accelerate local degradation [21]. These structural and interfacial aspects strongly influence the efficiency of the electrochemical reactions occurring at both electrodes.

2.1.2. Porous transport layers

Porous transport layers (PTLs), also known as Gas Diffusion Layers (GDLs), are positioned between the catalyst layers and the bipolar plates. PTLs perform several critical functions, including providing a conductive pathway for electrons between the catalyst layer and the bipolar plate, facilitating the distribution of water to the catalyst layer, and aiding in the removal of generated gases from the reaction sites. Additionally, PTLs offer structural support to the MEA and assist in heat dissipation to maintain optimal operating temperatures. Material requirements for PTLs include high electrical conductivity, chemical stability to resist corrosion in acidic and oxidative conditions, mechanical strength, and optimized porosity and pore structure. On the anode side, titanium-based Ti materials are commonly used due to their corrosion resistance and mechanical properties [22]. These are available in forms such as sintered titanium powders, titanium felt, and titanium foam. On the cathode side, carbon-based materials similar to those used in PEM fuel cells are often employed, as the environment is less corrosive. Design considerations for PTLs involve balancing porosity and pore distribution to ensure efficient gas removal and water distribution. Larger pores facilitate gas removal but may reduce mechanical strength and electrical contact, while smaller pores enhance capillary action for water distribution but may impede gas flow [23]. Recent advancements include the use of additive manufacturing (3D printing) to create tailored microstructures with precise control over porosity and pore architecture, optimizing performance [24]. Additionally, surface treatments and coatings are being developed to enhance corrosion resistance and electrical conductivity. A recent study proposed a woven titanium mesh filled with titanium powder as a hybrid PTL, which significantly outperformed conventional woven meshes while lowering PTL cost by more than 90 %

compared to titanium felt or sintered Ti. The performance gains were attributed to improved catalyst–PTL interfacial contact, graded porosity, and enhanced electron/bubble pathways, underscoring the dual role of PTL design in both durability and cost reduction [25].

2.1.3. Bipolar plates

Bipolar Plates (BPs) are essential components that perform several vital functions within a PEM electrolysis cell. They conduct electrical current across the cell with minimal resistive losses, contain flow channels for the uniform distribution of water to the anode, and facilitate the removal of gases from both electrodes. BPs also provide mechanical integrity and maintain uniform compression of the cell components, as well as aid in heat distribution and removal to maintain consistent operating temperatures. The material requirements for BPs include high electrical conductivity, corrosion resistance in acidic and oxidative conditions, mechanical strength, and gas impermeability to prevent leakage and cross-contamination of gases. Titanium is the most widely used material for BPs in PEM electrolysis due to its excellent corrosion resistance and mechanical properties [8]. However, titanium is expensive and can form a passive oxide layer that increases contact resistance. To mitigate this issue, surface coatings, such as noble metal coatings (e.g., gold or platinum), are employed to reduce contact resistance and enhance corrosion resistance, although they significantly increase costs [26]. Alternative approaches include using stainless steel with protective coatings to prevent corrosion and passivation under different operation conditions [27]. Design optimization of BPs focuses on flow field design, optimizing the geometry of flow channels to ensure uniform distribution of reactants, effective removal of products, and minimal pressure drops [28]. Advanced manufacturing techniques enable the creation of intricate flow channel geometries that enhance gas and liquid transport efficiency while maintaining structural integrity.

2.2. Stack and Balance of Plant

A PEM electrolysis system comprises multiple cells assembled into a stack and the Balance of Plant (BoP). The stack serves as the core where electrochemical reactions occur, while the BoP includes auxiliary systems to ensure the stack's efficient and safe operation. The stack consists of multiple cells connected in a bipolar configuration, where cells are electrically connected in series. This arrangement ensures that the same current passes through each cell, and the total voltage is the sum of the voltages of individual cells, offering advantages such as compact design and higher operating voltages [29].

The BoP encompasses key components that regulate temperature, pressure, and water flow rate, while also delivering reactants to the stack and removing generated products. Although there is no standard layout for PEM electrolysis systems, various configurations are documented in the literature [30, 31, 32]. The stack comprises approximately 45 % of the entire PEM water electrolysis system cost, with the BoP accounting for the remaining 55 % [17]. Within the cell, bipolar plates and the gas diffusion layer are among the most expensive components, representing 53 % and 17 %, respectively, of the total PEM cell cost, while the MEA accounts for about 24 % [17].

A schematic architecture that reveals the interaction of the stack with the BoP can be seen in Fig. 4. The key elements of the BoP include:

- **Power Supply System**: Delivers the required electrical energy to initiate the water-splitting process. Usually linked to the DC bus or renewable energy sources such as photovoltaic or wind power plants, DC/DC converters are sometimes useful for regulating the operating range of the PEMWE.
- **Water Management System**: Supplies purified water to the anode and includes components such as pumps, deionizers, flow meters, and water separators. A pump facilitates the circulation of water throughout the stack. Additionally, a deionizer ensures water purity by removing heavy metal cations that could originate from the BoP or as corrosion products within the stack.
- **Gas Handling System**: Equipped with separators and purifiers at the PEMWE outlets, this system separates the produced hydrogen and oxygen gases from the water. The separated gases are then directed to storage processes, while excess water is recirculated back into the water management circuit.
- **Thermal Management System**: Maintains optimal operating temperatures through heat exchangers, cooling loops, or heaters, ensuring efficient and reliable performance.
- **Control and Monitoring Systems**: Utilize sensors to measure temperature, pressure, mass flow, voltage, current, and water conductivity across the entire electrolysis system. Advanced control systems optimize performance and ensure safe operation by adjusting operational parameters in real time.

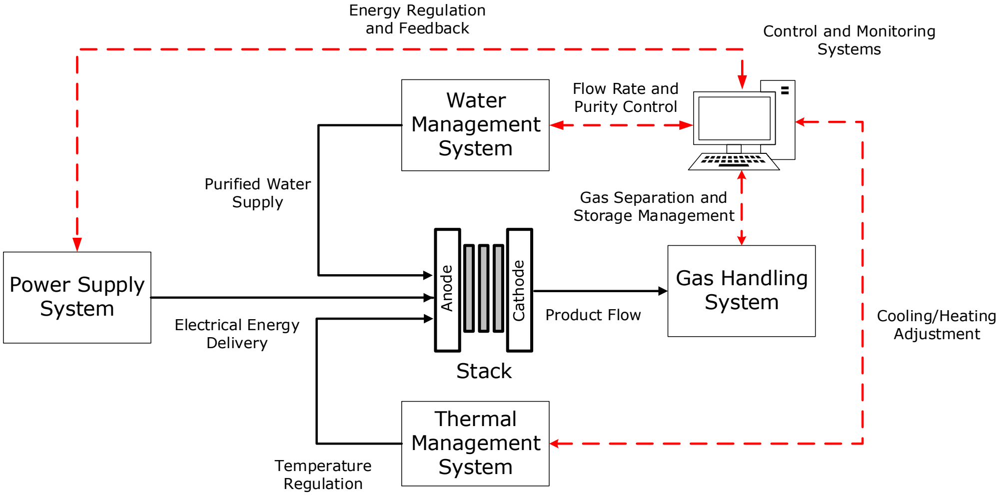


Figure 4: Schematic overview of key components and their interactions in a PEM electrolysis system

Manufacturers and commercial systems have expanded rapidly, driven by the global demand for green hydrogen. Key manufacturers include Nel Hydrogen, Hydrogenics (part of Cummins Inc.), ITM Power, H-TEC Systems, and Siemens Energy, among others. These companies offer PEM electrolysis systems ranging from small-scale units to large-scale installations with capacities reaching 100 MW. Emphasizing efficiency, reliability, and seamless integration with renewable energy sources. An illustrative example of a PEM electrolysis system layout, featuring two 1 MW stacks operating in parallel along with their associated Balance of Plant components (adapted from Hyfindr company), is presented in Fig. 5. This commercial system is scalable and can reach a power output of up to 5 MW, producing hydrogen at a rate of up to 2000 kg/day.

Having established a detailed understanding of the materials and system components that constitute a PEM electrolysis, we now turn our attention to the performance criteria and degradation mechanisms that critically impact their efficiency and longevity. Grasping these degradation processes is essential within our Integrated Optimization Framework (Fig. 2), as it lays the groundwork for developing accurate models. By examining how material properties and operational conditions contribute to degradation, these insights directly support strategies that sustain optimal operation of PEM electrolysis. The next section explores these degradation mechanisms in depth, providing essential insights for enhancing system durability and performance.

3. Performance criteria and degradation mechanisms of PEM Electrolysis

Optimizing the efficiency, durability, and overall performance of PEM electrolysis is essential for advancing hydrogen production technologies. A key approach to address this challenge is through the study of failure mechanisms associated with different materials utilized in PEM electrolysis. However, there remains a lack of comprehensive research on degradation mechanisms within the field of PEM electrolysis. As a result, the causes of degradation often rely on observations and findings from PEM fuel cell research. This is due to the similarities in the operating principles and materials used in both processes. While these assumptions can provide some useful insights, it is important to note that the conditions and operating environments in PEM electrolysis may differ from those in PEM fuel cells. Therefore, further research is necessary to fully understand the degradation mechanisms in PEM electrolysis and develop effective strategies to enhance the durability of the materials used in this process. Accelerated Stress Tests (AST) are a common method used to evaluate the durability of PEM electrolysis. These tests involve applying high levels of stress on both the cathode and anode sides of the system for a short period, to accelerate the failure processes that would typically occur at lower stress levels over a longer duration. Briefly, these tests are cost-effective and time-saving methods for evaluating the performance and durability of materials used in PEM electrolysis.

The existing literature includes comprehensive reviews by Feng et al. [33] and Khatib et al. [34], which delve into the various aspects of material degradation in PEM electrolysis. These reviews offer valuable insights into the factors

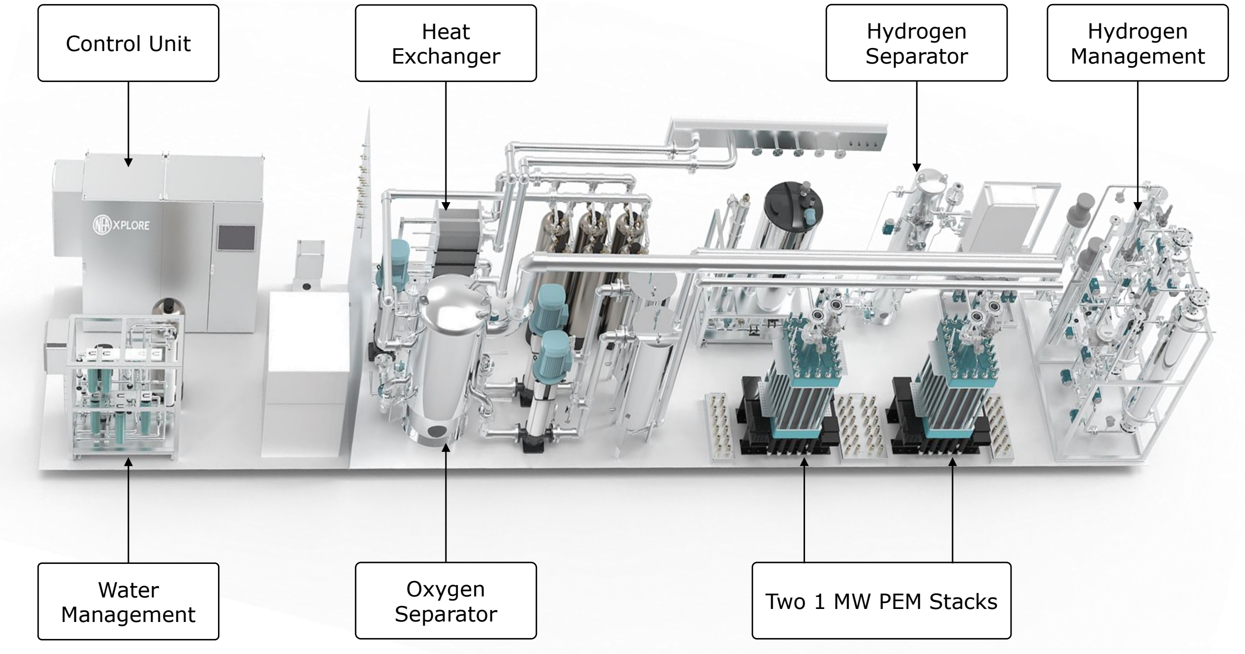


Figure 5: Schematic architecture of a commercialized PEM electrolysis system contains two 1 MW stacks in parallel

that influence degradation and present effective strategies for enhancing the durability of the materials employed in this process. Additionally, Shirvanian and Berkel [35] introduced a mini-review that examines the current status of cell components and their durability. These reviews highlight the importance of understanding degradation mechanisms and developing effective strategies to enhance the durability of materials used in PEM electrolysis as well. Recently, Kuhnert [36] conducted a review on the ASTs, exploring the effects of different operational conditions on the PEM electrolysis operation. This review provides insights into the optimal testing conditions for evaluating the durability of materials used in PEM electrolysis under different operating conditions.

This section reviews the different cell components, summarizing the prominent degradation mechanisms and their causes for each component.

3.1. Membrane

Nafion, a perfluorosulfonic acid (PFSA) polymer, is the most established membrane material due to its excellent proton conductivity and chemical stability [37]. However, compared to other components, the membrane is considered one of the weakest components in terms of durability [38], with the majority of literature focusing on the degradation phenomena associated with it. Membrane degradation can be categorized into mechanical, chemical, and thermal degradation.

Mechanical degradation involves physical damage such as punctures, cracks, tears, or mechanical stresses applied to the membrane. Chemical degradation is mainly caused by metallic impurities that attack the membrane structure, while thermal degradation results from overheating during operation.

Stucki et al. [38] demonstrated that membrane thickness is a significant factor in MEA degradation, with the dissolution of the membrane observed more prominently on the cathode side where hydrogen reactions occur. The fluoride release rate (FRR) is a commonly used metric for quantifying and predicting the chemical degradation rate of PFSA membranes. Fouda-Onana et al. [39] investigated membrane thinning at different temperatures (60 °C and 80 °C) using a FRR characterization technique. Their results showed that increasing the temperature significantly accelerates membrane thinning, with rates of 11.5 nm/h at 80 °C and 2 nm/h at 50°C. They concluded that temperature has a predominant effect on membrane degradation compared to current density.

During operation, the generation of hydrogen peroxide can lead to the formation of radicals such as hydroxyl ($HO^{\bullet}$) and hydroperoxyl ($HOO^{\bullet}$) through reactions with metal divalent ions. These radicals aggressively attack the membrane, damaging the PFSA structure. Grigoriev et al. [40] studied MEA degradation using Nafion membranes and observed a short circuit after 5,500 hours of operation. Post-mortem analysis revealed that the MEA lost over 75% of its initial thickness (from 140 μm to 35 μm). The thinning was attributed to impurities such as Si, K, Ca, and Cu from the water feed, which facilitated hydrogen crossover to the anode side and subsequent hydrogen peroxide production. It was also reported that platinum is not a suitable anode catalyst material due to its instability within the voltage range.

Millet et al. [41] observed membrane perforation in a Nafion 117 membrane within a cell stack, leading to a short circuit. The exact cause of the temperature increase leading to perforation was not clearly identified, but possible explanations included hot spots from uneven current distribution and insufficient water supply causing membrane drying. Sun et al. [42] investigated long-term degradation and concluded that impurities detected on the membrane surface using Electron Probe Microanalysis (EPMA) were the main cause of the degradation. These impurities, originating from the water supply and auxiliary components, significantly affected ion transfer and increased potential on both electrodes.

3.2. Catalyst layer

The current state-of-the-art materials for catalysts in PEM electrolysis are iridium oxide (IrO_2) at the anode and carbon-supported platinum (Pt/C) at the cathode. The degradation of catalysts in PEM electrolysis can be attributed to three main causes: poisoning, dissolution, and agglomeration. Catalyst dissolution primarily occurs on the anode side of PEM electrolysis, where reactions happen in harsh environments and at high potentials. Specifically, the dissolution of iridium (Ir) catalysts significantly facilitates OER activity by decreasing the electrochemically active surface area. Grigoriev et al. [40] conducted an experiment to investigate catalyst degradation, in which Pt was used on both sides of the membrane to accelerate the degradation process. The study showed that nano-particles of Pt catalyst materials were present on the membrane surface. Cross-sectional analysis using transmission electron microscopy (TEM) revealed that the cathode did not dissolve, while the anode side was found to be dissolved. The dissolution of the anode was attributed to the high potential during the operation. This was also supported by [43] in which the dissolution of Ir was observed under cycling operating potentials between open circuit voltage (OCV) and (1.6 V). Lettenmeier et al. as well [44], observe the diffusion of dissolved iridium through the membrane surface using scanning electron microscopy (SEM), while operating at high current densities (between 0.15 $mA.cm^{-2}$ and 4 $mA.cm^{-2}$) in a period of 800 h, this proves that high current densities (i.e., high potentials) or load cycling (OCV) speed up the dissolution of Ir. Furthermore, Alia et al. [45] notice that the high-frequency cycling has more effect on the Ir geometry than the voltage hold, and the dissolution of the Ir depends strongly on the material load of the electrode. When the catalyst loading increases, the degradation rate decreases [46].

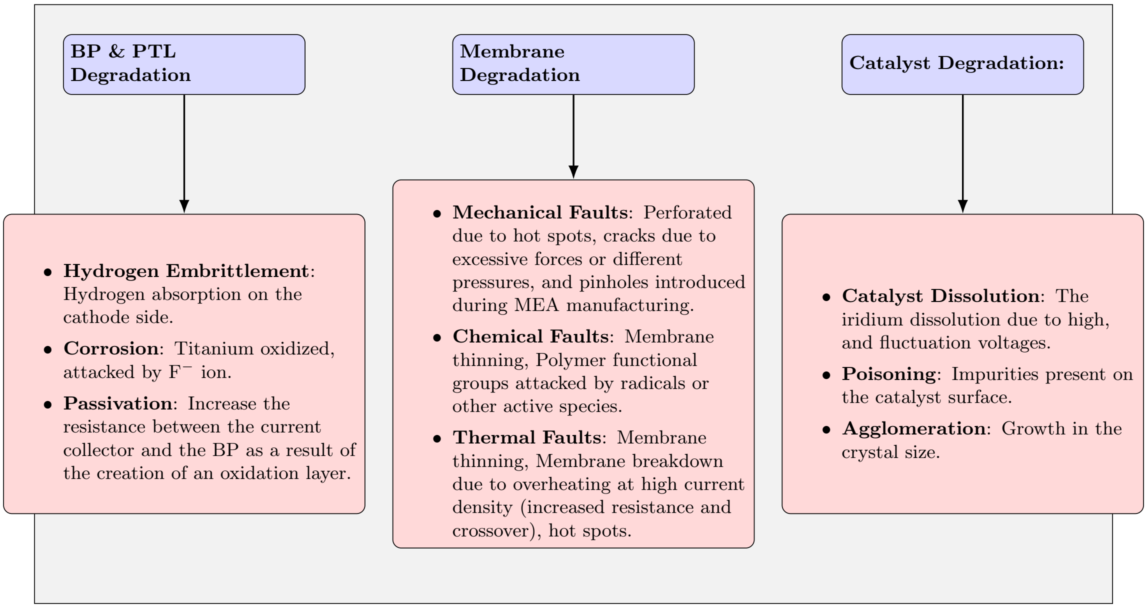
Despite being a relatively stable HER electrocatalyst, studies have shown that Pt particles still suffer from catalyst particle aggregation [47, 48]. The reasons for Pt particle agglomeration in PEM electrolysis are not yet fully understood, and the explanations used for PEM fuel cells are often applied to electrolysis as well. Three major modes of particle growth exist in PEM fuel cells, which are Ostwald ripening, reprecipitation, and coalescence [49]. Overall, the contribution of the Pt agglomeration effect to global degradation is claimed to be insignificant and small compared to other degradation mechanisms [48].

Cationic contamination basically came from feed water or corrosion of metal components of the PEM, the circulated water may introduce some cationic impurities like Na^{+}, Ca^{+2}, Cu^{+2}, Ni^{+2}, Pb^{+2}, and Fe^{3+} [33]. These impurities can move and settle on the surfaces of the electrodes. Some cations with high potential can move to the cathode side and get reduced to metallic form, this can affect the surface of activity on the cathode side by reducing proton concentration and raising the over-potential. This degradation may be interpreted as a decrease in the exchange current density. Rakousky et al. [47] reported the presence of titanium particles on the cathode side, originating from the anode PTL and subsequently deposited in the cathode catalyst layer. This phenomenon caused elevated cell voltage and reduced exchange current density

3.3. Bipolar plate and porous transport layer

The state-of-the-art materials for the bipolar plate being used today are mainly titanium and stainless steel. The main degradations of the bipolar plates are hydrogen embrittlement, passivation, and corrosion. As the PTLs are exposed to conditions nearly identical to those of the bipolar plates, they have roughly the same failure mechanisms.

On the cathode side and because of the hydrogen environment, the embrittlement of the titanium material can take place. In this process, the hydrogen is absorbed by the titanium material, and this leads to the production of titanium hydride TiH_2. This could result in cracking and mechanical failure in titanium-based BPs, eventually leading



BP & PTL Degradation

- **Hydrogen Embrittlement**: Hydrogen absorption on the cathode side.
- **Corrosion**: Titanium oxidized, attacked by F^- ion.
- **Passivation**: Increase the resistance between the current collector and the BP as a result of the creation of an oxidation layer.

Membrane Degradation

- **Mechanical Faults**: Perforated due to hot spots, cracks due to excessive forces or different pressures, and pinholes introduced during MEA manufacturing.
- **Chemical Faults**: Membrane thinning, Polymer functional groups attacked by radicals or other active species.
- **Thermal Faults**: Membrane thinning, Membrane breakdown due to overheating at high current density (increased resistance and crossover), hot spots.

Catalyst Degradation:

- **Catalyst Dissolution**: The iridium dissolution due to high, and fluctuation voltages.
- **Poisoning**: Impurities present on the catalyst surface.
- **Agglomeration**: Growth in the crystal size.

Figure 6: Degradation Mechanisms in PEM Electrolysis Components

to component fracture. It was reported that nitride, carbon, or graphite coating can be applied to overcome the H_2 uptake [50][51].

Due to the high potential and strong acidic environments, passivation could occur, which can significantly raise the contact resistance between the bipolar plate and the PTL by producing an oxide film with low electrical conductivity. To overcome the passivation, noble metals like platinum or gold coatings are frequently used. However, it should be noted that this can significantly increase the cost. Therefore, it is essential to optimize these component designs by balancing performance and cost.

The corrosion of titanium is another degradation mechanism discussed in the literature for PEM electrolysis. However, this type of fault is in general not expected due to the operating condition of the electrolysis, besides that, the oxide film created because of passivation can be used as a shelter at some point to protect the titanium from corrosion. However, the corrosion can be occurred as a result of fluoride ions F^{-1} generation on the membrane, which can destroy the passivation layer, leading to more corrosion [8]. Stainless steels are known to have less embrittlement than titanium, but when operating at high potentials, stainless steel has significant corrosion issues [52].

Fig. 6 summarizes the different degradations associated with the different components of the PEM electrolysis system.

3.4. Degradation Rates

Building on the previously discussed degradation mechanisms, this subsection provides a quantitative analysis of PEM electrolysis degradation, focusing on how operational parameters influence voltage decay rates. Voltage decay is a critical metric as it reflects the gradual loss of efficiency and performance over time. Table 1 aggregates empirical data from various studies, illustrating the effects of current density, temperature, catalyst loading, and membrane type on voltage decay rates in PEM electrolysis. The data underscore the profound impact of material selection and operating conditions on both the performance and durability of PEM electrolysis.

Operational parameters such as current density and temperature strongly correlate with voltage decay rates. Higher current densities and elevated temperatures accelerate degradation processes. For example, operating at 2.0 A/cm^2 and 80 °C with RuO_2 at the anode and Pt/C at the cathode side with Nafion membranes resulted in a substantial voltage decay of $450\mu V/h$ over 300 hours [53]. In contrast, the system ran at 1 $A/cm^2$and exhibited minimal voltage decay of less than 330 $\mu V/h$ over the same period [53].

Xu et al. [54] compared constant and start–stop operating modes and reported a voltage loss equivalent to 4.5 % over 1000 h under constant operation, versus 2.5 % over the same period under start–stop cycling. These findings suggest that intermittent operation does not always accelerate degradation, and under certain conditions may mitigate stress accumulation compared to steady-state operation. Su et al. [55] showed that degradation strongly depends on the operating mode at 80 °C. Under constant-current operation, the voltage rise increased with current density (from $\sim 23\ \mu V/h$ at 1 A/cm^2 to $\sim 50\ \mu V/h$ at 3 A/cm^2). In narrow square-wave cycling (1–2 A/cm^2), longer step times reduced degradation, whereas in wide cycling (1–3 A/cm^2) the opposite trend was observed, with degradation rates increasing at higher currents and longer steps. This stark difference emphasizes the detrimental effects of high current densities on system durability. In addition, more recent investigations have provided quantitative insights into degradation behavior under different material configurations. For instance, catalyst loading plays a pivotal role in mitigating voltage decay. Higher loadings of IrO_2 and the incorporation of TiO_2 in the anode catalyst layer, as demonstrated by Rakousky et al. [56], correlate with lower voltage decay rates, reaching as low as $15.85\mu V/h$. Beyond loading effects, even the microstructural design of the IrO_x catalyst has been shown to significantly influence degradation behavior. Zhang et al. [57] reported that a tunnel-structured IrO_x anode with a low Ir loading of approximately 0.28 mg/cm^2 could sustain operation at 2.0 A/cm^2 and 80 °C for 1800 h with an average voltage rise of only 7 $\mu V/h$, whereas a reference IrO_x morphology at the same loading exhibited a much higher degradation rate of $230\mu V/h$. This finding highlights that, in addition to catalyst quantity, the intrinsic nanostructure of the active phase plays a crucial role in achieving long-term stability under demanding conditions. LaConti et al. [58] reported an exceptionally low average degradation rate of 1.91 μV/h by employing a high catalyst loading of 4 mg/cm^2 on each side of the membrane. This highlights the significance of catalyst loading in enhancing electrode stability and minimizing material loss. Under consistent operating conditions of 0.10 A/cm^2 and 80 °C, increasing the anode catalyst loading from 0.10 mg/cm^2 IrO_2 to 0.32 mg/cm^2 IrO_2 resulted in a reduction of voltage decay from 180 $\mu V/h$ to 110 $\mu V/h$ over 1000 h of operation. Furthermore, the incorporation of TiO_2 alongside 0.12 mg/cm^2 IrO_2 significantly enhanced stability, achieving a minimal voltage decay of just 20 $\mu V/h$ within the same timeframe [19]. The cathode load is less demanding, where a loading rate of 0.10 mg/cm^2 is reached in multiple studies. Material configuration of PTL has also been shown to strongly impact durability. A novel hybrid PTL based on woven titanium mesh filled with titanium powder reduced the irreversible voltage decay rate by 39.3% during an 800 h AST test, corresponding to a decrease of approximately 121 $\mu V/h$ compared with a conventional titanium mesh design [25]. The type of membrane used together with the catalysts also significantly influences degradation outcomes. Systems utilizing robust membranes such as Aquivion E100-09S with higher IrRuOx and titanium loadings showed lower voltage decay rates (ranging from 5 to 23 $\mu V/h$) under identical current densities compared to those using Nafion membranes [59]. This highlights the importance of selecting membranes with superior mechanical and chemical stability to improve overall system durability.

The interplay between current density, temperature, catalyst loading, and membrane type reveals that optimizing these parameters is crucial for balancing hydrogen production rates with system longevity. High current densities and temperatures accelerate degradation processes, while adequate catalyst loadings and robust membrane selections mitigate these effects, thereby enhancing overall performance and lifespan.

Understanding the identified degradation mechanisms and the used materials provides a crucial foundation for developing accurate modeling methods and paving the way to maintain optimal operation throughout the system's lifetime, as indicated in our Integrated Optimization Framework (Fig. 2). By comprehending how degradation occurs, we can create models that simulate and predict the behavior under various operating conditions. The following section explores various modeling techniques used to simulate PEM electrolysis operation, providing insights into system behavior and guiding subsequent optimization efforts.

Table 1
Degradation Characteristics of PEM Electrolysis Under Different Operating Conditions

Current	Anode	Cathode	Membrane	Time Period	Voltage Decay	Reference
1 A/cm^2 @ 55 °C	3 mg/cm^2 IrRuOx	3 mg/cm^2 Pt black	Aquivion E098-09	5000 h	<3 µV/h	[60]
2.0 A/cm^2 @ 80 °C	2.3 mg/cm^2 IrO_2	1.0 mg/cm^2 Pt/C	Nafion	500 h	286.1 µV/h	[61]
0 A/cm^2 to 2.0 A/cm^2 (100 s each)	2.3 mg/cm^2 IrO_2	1.0 mg/cm^2 Pt/C	Nafion	500 h	36.7 µV/h	[61]
0 A/cm^2 to 2.0 A/cm^2 (10 s each)	2.3 mg/cm^2 IrO_2	1.0 mg/cm^2 Pt/C	Nafion	500 h	−53.5 µV/h	[61]
1 A/cm^2 to 2 A/cm^2 (6 h each)	2.25 mg/cm^2 IrO_2 & TiO_2	0.8 mg/cm^2 Pt/C	Nafion 117	1009 h	65.41 µV/h	[56]
0 A/cm^2 to 2 A/cm^2 (6 h each)	2.25 mg/cm^2 IrO_2 & TiO_2	0.8 mg/cm^2 Pt/C	Nafion 117	1009 h	15.85 µV/h	[56]
0 A/cm^2 to 2 A/cm^2 (10 min each)	2.25 mg/cm^2 IrO_2 & TiO_2	0.8 mg/cm^2 Pt/C	Nafion 117	1009 h	49.55 µV/h	[56]
1.35 A/cm^2 @ 50 °C	2 mg/cm^2 Pt & Ir	4 mg/cm^2 Pt/C	Nafion 110	2000 h	1.5 µV/h	[32]
1 A/cm^2 @ 80 °C	0.4 mg/cm^2 IrO_2	0.2 mg/cm^2 Pt/C	Nafion 212	122 h	230 µV/h	[62]
2 A/cm^2 @ 80 °C	1.2 mg/cm^2 RuO_2	0.18 mg/cm^2 Pt/C	Nafion	300 h	450 µV/h	[53]
1 A/cm^2 @ 80 °C	1.2 mg/cm^2 RuO_2	0.18 mg/cm^2 Pt/C	Nafion	300 h	330 µV/h	[53]
0.5 A/cm^2 @ 60 °C	1.5 mg/cm^2 Ir black	0.4 mg/cm^2 Pt/C	Nafion 115	7800 h	35.5 µV/h	[42]
1 A/cm^2 @ 80 °C	0.10 mg/cm^2 IrO_2	0.25 mg/cm^2 Pt/C	Nafion 115	1000 h	180 µV/h	[19]
1 A/cm^2 @ 80 °C	0.32 mg/cm^2 IrO_2	0.25 mg/cm^2 Pt/C	Nafion 115	1000 h	110 µV/h	[19]
1 A/cm^2 @ 80 °C	0.12 mg/cm^2 IrO_2 & TiO_2	0.25 mg/cm^2 Pt/C	Nafion 115	1000 h	20 µV/h	[19]
2 A/cm^2 @ 80 °C	2.25 mg/cm^2 IrO_2TiO_2	0.8 mg/cm^2 Pt/C	Nafion 117	1000 h	194 µV/h	[47]
1 A/cm^2 @ 90 °C	2.5 mg/cm^2 Pt	2.5 mg/cm^2 Vulcan/Pt	Nafion 115	5500 h	3.84 mV/h	[47]
1.44 A/cm^2 @ 90 °C	4 mg/cm^2 Pt-Ir	4 mg/cm^2 Pt	Nafion 120	32 630 h	1.91 µV/h	[58]
1 A/cm^2 @ 80 °C	1.27 mg/cm^2 IrRuOx, Ti	0.1 mg/cm^2 Pt/C	Aquivion E100-09S	1000 h	5 µV/h	[59]
3 A/cm^2 @ 80 °C	1.27 mg/cm^2 IrRuOx, Ti	0.1 mg/cm^2 Pt/C	Aquivion E100-09S	1000 h	11 µV/h	[59]
1 A/cm^2 @ 80 °C	0.34 mg/cm^2 IrRuOx, Ti	0.1 mg/cm^2 Pt/C	Aquivion E100-09S	1000 h	15 µV/h	[59]
3 A/cm^2 @ 80 °C	0.34 mg/cm^2 IrRuOx, Ti	0.1 mg/cm^2 Pt/C	Aquivion E100-09S	1000 h	23 µV/h	[59]

4. Modeling methods for optimal operations

Predicting the system performance over time is critical in understanding and optimizing PEM electrolysis systems. PEM electrolysis is a complex multi-physics process with tightly coupled subsystems; accurate models are indispensable for identifying the operating regimes that maximize efficiency and durability. While auxiliary system modeling is relatively mature, modeling techniques at the PEM cell and stack levels, where most efficiency losses and degradation originate, are still insufficiently developed. Strengthening these models is therefore essential for achieving optimal operation, as they provide the predictive capability needed for real-time control, degradation-aware scheduling, and long-term performance optimization.

Modeling of PEM electrolysis can be broadly divided into two main parts: the electrochemical model and the governing equations dedicated to modeling the transport processes. In this section, we present a comprehensive review of the different models proposed in the literature and discuss their implications for optimal operations.

4.1. Electrochemical model

Water electrolysis is a non-spontaneous process that can be achieved by applying a specific amount of voltage to both sides of the electrode. The electrochemical sub-model is mainly represented by the voltage of the cell and depends on various parameters such as current, temperature, pressure, and cell geometry. In the literature, the electrochemical model has received the utmost attention in investigating the performance of the PEM electrolysis. Multiple models have been proposed, which can be categorized into static and dynamic models, as discussed in the following section:

4.1.1. Static model

The static model describes a system's physics without tracking changes over time. It can be either semi-empirical- using equations based on semi-physical laws, or empirical, relying on equations without physical justification.

Semi-empirical model One of the earliest semi-empirical PEM electrolysis models (1991) examined voltage-current relationships and temperature effects [63]. A more comprehensive model introduced by Choi [64] (2004) employed the Butler–Volmer equation for activation overpotential, an empirical expression for the reversible potential, and a constant membrane resistance for ohmic losses. Most subsequent semi-empirical models have followed Choi's framework.

The total energy needed to split water molecules is called the Gibbs free energy and is expressed as follows [65]:

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

ΔH is the thermal energy requirement, ΔS is the entropy charge, T is the temperature.
The link between electrical and chemical energy required for water splitting is represented as follows [66]:

$$V_{cell} = -\frac{\Delta G}{nF} \tag{2}$$

where V_{cell} is the electrolysis cell voltage, n is the number of electrons transferred during the reaction, and F is the Faraday constant, it can be seen that the voltage is proportional to Gibbs free energy, which is dependent on the temperature by means of the enthalpy.
By taking into account the overvoltage losses caused by kinetic losses in electrolyte layers and ohmic losses, the total voltage that must be applied to electrolysis can be expressed as follows: [30]

$$V_{cell} = V_{rev} + V_{cons} + V_{act} + V_{ohm} + V_{bub} \tag{3}$$

V_{rev} is the reversible voltage, V_{act} is the activation voltage, V_{ohm} is the ohmic voltage, V_{cons} is the concentration overpotential, and V_{bub} is the voltage caused by the bubble effect.

Reversible voltage The reversible voltage is the minimum voltage required to split water into hydrogen and oxygen at a given temperature and pressure, assuming perfect reversibility and no energy losses. V_{rev} can be expressed using the Nernst equation as follows[11]

$$V_{rev} = V_0 + \frac{RT}{2F}\ln\left(\frac{P_{H2}\sqrt{P_{O_2}}}{P_{H_2O}}\right) \tag{4}$$

V_0 is the standard reversible potential, R the gas constant, P_{H_2}, P_{O_2}, P_{H_2O} are the partial pressures of hydrogen, oxygen, and water, respectively. Too many empirical formulae were proposed in the literature to represent V_0, one of the most used formulae was proposed by Bernardi and Verbrugge in the early 90s for the fuel cell, but several authors use it for the PEM electrolysis as well, and it's expressed as follows [67]

$$V_0 = 1.229 - 0.9 \times 10^{-3} (T - 298.15) \tag{5}$$

Activation voltage drop To initiate the electrolysis reaction, some potential must be applied to the anode and the cathode. This potential is referred to as the required potential to activate the chemical reactions at both electrodes. The change in this voltage depends on the temperature and can be determined by applying the Butler-Volmer equation, which takes into account the kinetics of the charge transfer reaction. The activation voltage on both electrodes is expressed as follows: [16, 68]

$$V_{act,an} = \frac{RT}{\alpha_{an} F} arcsinh\left(\frac{j}{2j_{0,a}}\right) \tag{6}$$

$$V_{act,c} = \frac{RT}{\alpha_{cat} F} arcsinh\left(\frac{j}{2j_{0,c}}\right) \tag{7}$$

The two equations can be simplified as follows (Tafel's equation): [69]

$$V_{act} = \frac{RT}{\alpha n F} \ln\left(\frac{j}{j_0}\right) \tag{8}$$

This equation can be used on both sides (anode and cathode). j represents the current density. The coefficient $\frac{RT}{\alpha n F}$ is known as Tafel's slope, and it is often used to investigate the rate-determining step of the electrode reaction, providing valuable insight into electrochemical mechanisms. The parameter α, known as the charge transfer coefficient, and usually confined between 0 and 1 and often takes the value 0.5 for elementary reactions. However, many researchers revealed that α is not fixed and depends on temperature changes. In [70], Marangio used the values 2 and 0.5 for the charge transfer coefficient on the anode and the cathode side, respectively, and the model was successfully validated. Other suggested values can be found on Flacao review [71].

The parameters $j_{0,a}$ and $j_{0,c}$ represent the exchange current densities of the anode and cathode, respectively. These values quantify the intrinsic reaction rates at equilibrium. Falcão et al. [71] reported that the exchange current densities at the cathode are generally higher than at the anode, which indicates that the cathodic kinetics are faster.

The mass transport overpotential The mass transport overpotential, also known as the diffusion or concentration overpotential-becomes more significant at high current densities. These losses arise from variations in the concentration of reactants at the electrode surface during electrolysis. The resulting concentration voltage can be calculated for both the anode and cathode using the Nernst equation, as follows: [70]

$$V_{cons,an} = \frac{RT}{2F} ln\left(\frac{C_1}{C_0}\right) \tag{9}$$

where C_1 is the concentration of oxygen or hydrogen, and C_0 is the concentration taken as the reference concentration. Another equation is frequently used to describe the diffusion overpotential depends on j_{lim}, which is the maximum current that the electrolysis can receive, and it is expressed as follows [11]:

$$V_{cons} = \frac{RT}{\beta n F} \ln\left(1 + \frac{j}{j_{lim}}\right) \tag{10}$$

Ohmic voltage drop The ohmic loss arises from the resistive contributions of the bipolar plates, PTL, and membrane. Fritz et al. [68] described individual ohmic losses in each component, while Han et al. [72] introduced an equivalent circuit model to separate resistances throughout the cell. However, accurately determining each component's dimensions for precise resistance values can be challenging. The overall ohmic loss is given by:

$$V_{ohm} = V_{ohm,a} + V_{ohm,c} + V_{ohm,m} \tag{11}$$

Often, the membrane's resistivity dominates among cell components, making it the primary focus. The following equation describes the membrane's resistivity [69, 73, 71]:

$$R_{mem} = \frac{\delta}{\sigma_m} \tag{12}$$

Equation 12 shows that membrane resistance increases with the thickness (δ); hence, a thinner membrane improves PEM electrolysis efficiency. The conductivity σ is expressed as follows for the case of Nafion membrane[71][72]:

$$\sigma_m = (0.005139\lambda_m - 0.00326)exp\left[1268\left(\frac{1}{303} - \frac{1}{T}\right)\right] \tag{13}$$

λ_m denotes the degree of membrane humidification, which can be expressed as a function of the water activity as follows [74]:

$$\begin{cases} \lambda = 0.043 + 17.81a - 39.85a^2 + 36a^3 & 0 < a < 1 \\ \lambda = 14 + 1.4(a-1)^3 & 1 < a \end{cases} \tag{14}$$

Alternative expressions for σ_m are provided in [74]. In PEM electrolysis, the membrane is generally assumed to be fully hydrated because water is continuously supplied. In practice, the membrane's water content (often quantified by the degree of humidification) typically ranges from 14 to 25, depending on the specific membrane material.

Bubble effect The formation of bubbles in electrolysis involves three steps: nucleation, growth, and departure [75, 76**?**]. Bubble accumulation reduces the active surface area for catalysis, influencing the cell's overall potential. Numerous approaches exist to calculate the coverage area. Vogt et al. [77] proposed a straightforward formula relating bubble coverage area to the current:

$$\Theta = \left(\frac{j}{j_{\Theta\to 0}}\right)^{0.3} \tag{15}$$

where $j_{\Theta\to 0}$ is the current density at full bubble coverage state. However, it is important to note that parameters other than the current may also impact the coverage area. Recently, Vogt et al. [78] developed an improved equation that takes into account current, pressure, temperature, bubble detachment, and residence time. Bubble dynamics are also affected by factors such as surface wettability and electrode design, as well as external forces like magnetic fields and mechanical vibrations [79, 80]. Zerrougui et al. [81] proposed a model based on force balance, using the calculated bubble radius to estimate coverage; this model was experimentally validated.

Bubble coverage can significantly affect cell performance by reducing available active sites, which in turn increases the current density. Equations 16 provide the estimation of both the new active site area and the resulting current density, as proposed by Vogt et al. [77].

$$A = A_0 - \Theta \quad j = j_0\frac{A_0}{A} \tag{16}$$

The coverage of bubbles can significantly impact the overall performance of cells by exerting influence on different segments of the polarization curve. These include the activation overpotential ($V_{act,cov}$), the ohmic losses ($V_{ohm,cov}$), and the concentration overpotential ($V_{conc,cov}$) [82, 83, 84]. A summary of the equations and the effects of bubbles on each part of the polarization curve is provided in Table 2

Empirical model The empirical model consists of the investigation of the physical behavior process of the system via a bunch of collected data, and makes it fit in a proposed empirical equation that connects a number of variables, which may not necessarily have a physical meaning. Such models have also been used to represent PEM electrolysis, offering a simplified way to capture electrochemical behavior. Various correlation-based empirical equations exist in the literature, many tracing back to Griesshaber and Sic [85], where the voltage across a single cell is written as:

$$V_{cell} = V_{rev} + \frac{r}{A}I + s\log\left(\frac{t}{A}I + 1\right) \tag{17}$$

Voltage losses equation	Bubble effect
$V_{act,cov} = \frac{RT}{F}\ln\left(\frac{1}{1-\Theta}\right)$	Increasing the coverage area may result in higher current density, leading to an increase in the activation overpotential
$V_{co,cov} = \frac{RT}{2F}\ln\left(\frac{\left[H^{+}\right]_{a}^{2} p_{H_2,c}\sqrt{p_{O_2,a}}}{[H^{+}]_{c}^{2}}\right)$	Bubble can reduce the concentration overpotential by absorbing dissolved gases and lowering the level of supersaturation in the electrolyte
$V_{ohm,cov} = \frac{iL(1-K_m)}{\sigma_m K_m}$	The presence of bubbles on electrode surfaces and in the electrolyte can cause an increase in ohmic overpotential by impeding the transport of current between electrodes

Table 2
Voltage losses caused by bubbles and their effect [83, 82]

r is the ohmic resistance of the cell, s and t are overvoltages coefficients, A is the surface of the membrane,I is the current through the cell.
Years later, Ulleberg [86] refined this model to better capture the overpotentials, incorporating temperature effects on both overpotential and ohmic resistance in the revised equation:

$$V = V_{rev} + \frac{r_1 + r_2 T}{A} I + (s + s_1 T + s_2 T^2)\log\left(\frac{t_1 + t_2 T + t_3 T^2}{A} I + 1\right) \tag{18}$$

To enhance the equation's accuracy, Sánchez et al. [87] incorporated the effect of pressure, resulting in an updated form of equation 18 as follows:

$$V = V_{rev} + \frac{(r_1 + d_1) + r_2 T + d_2 P}{A} I + (s + s_1 T + s_2 T^2)\log\left(\left(t_1 + \frac{t_2}{T} + \frac{t_3}{T^2}\right) I + 1\right) \tag{19}$$

Where r_1, r_2, d_1, d_2, s, s_1, s_2, t_1, t_2, and t_3 known as empirical parameters are constants and can be numerically calculated using non-linear regression techniques.

4.1.2. Dynamical model

Dynamical models describe how a system's physical behavior evolves over time. Only a limited number of such models address PEM electrolysis, and most rely on equivalent electrical circuits, which are particularly useful for current-based control (e.g., coupling PEM with converters). Da Silva et al. [88] proposed a circuit model in which the anode and cathode activation overpotentials are represented by parallel resistor-capacitor elements, ohmic losses by a resistor, and the reversible power by a DC voltage source. Koundi [89] developed a similar model, where the state space representation was established and the system was controlled using the sliding mode technique. Another model was introduced by Guilbert et al. [90], where a model that describes the static-dynamic model for one cell was developed and validated. A capacitor in parallel with a resistor was used to present the dynamics activation overvoltages on the anode and the cathode sides, separately; a resistor represented the ohmic overpotential of the membrane, and a DC voltage source represented the reversible overpotential. More recently, Hernández et al. [91] built another equivalent circuit to study the dynamic response of a PEM electrolysis stack under rapid current transients. A recent study by [92] introduced a generic equivalent circuit model for PEM electrolysis, parameterized by in-situ electrochemical impedance spectroscopy. The model simulates both current- and voltage-controlled modes, accurately capturing steady-state and transient behaviors across start-up, operation, and shut-down. By integrating diode switching and RC dynamics, it reproduces multi-time-scale electrical responses and provides a practical tool for power electronics design and control. Alongside these, Ratib et al. [93] presented a comprehensive review of electrical-circuit PEMWE models that summarize RC activation blocks and ohmic elements used to reproduce voltage dynamics and guide control design.

A general representation of the PEM electrolysis circuit is shown in Fig. 7. It should be noted that these circuit models often neglect ensemble dynamics arising from physical processes other than electrochemistry. This could result in inconsistencies in the model results when a multiphysics model is built.

Dynamic models are essential for understanding transient behaviors and developing control strategies. However, their complexity and the requirement for detailed parameter information limit their widespread application. Future

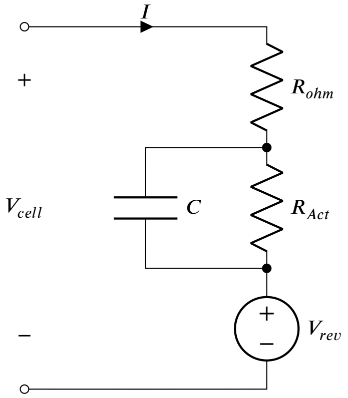


Figure 7: General representation of the electrical equivalent circuits for the PEM electrolysis

Table 3
Summary of Modeling Approaches and Simulation Software in Literature

Reference	1D	2D	3D	Simulation tools	Comments
[94]	★			COMSOL Multiphysics	Study the effect of CL loading and PTL parameters on PEM electrolysis
[95]	★			MATLAB	Dynamic modeling for high pressure PEM
[96]		★		Fluent	Study the effect of PTL parameters on the PEM performance
[97]		★		COMSOL Multiphysics	Study the effect of water velocity on oxygen bubbles
[98]			★	OpenFOAM	Study the gas-water transport on the channels
[99]			★	OpenFOAM	Gas and water flow in the channels
[100]			★	ANSYS FLUENT	Two-phase flow in the anode channel
[101]			★	/	Compare different flow field design
[102]			★	OpenFOAM	Study the oxygen bubbles dynamics

research should be focused on developing more comprehensive and accurate dynamic models that can be validated against experimental data, thereby enhancing their utility in operational optimization.

4.2. Modeling approaches for transport processes in PEM electrolysis

Governing equations, often in partial differential form, are fundamental for deriving models that describe the physical phenomena of heat transfer, mass and charge transport, and species interactions in PEM electrolysis systems. Numerous research studies have investigated electrolysis cells' transport dynamics and thermal behavior, which significantly impact system performance [81]. As a result, a wide range of models has been proposed in the literature, ranging from simple zero-dimensional formulations to complex multidimensional representations. A table that summarises some of the existing models in literature with the different dimensions and different simulation tools used can be seen in Table 3.

4.2.1. Zero-Dimensional models

The simplest and most commonly used models assume zero dimensions, treating the PEM electrolysis system as a closed volume that receives heat and fluid. Gorgun et al. [103] presented a dynamic model based on mole conservation on the anode and cathode sides. Their model aimed to study mass transport inside the MEA, including the electro-osmotic effect and diffusion through the membrane, and incorporated dynamic hydrogen storage. However, the model neglected the effects of heat transfer and mass transfer caused by different pressures on both electrode sides and was not experimentally validated. Awasthi et al. [104] developed a similar model that considers mass transport in the MEA.

They simulated the model using Matlab/Simulink software and validated it against experimental data, demonstrating good agreement with the experimental results. Yigit et al. [105] further extended the model to encompass auxiliary components of the PEM system, such as the water pump, cooling fan, power supply, controller, sensors, and storage tank. The proposed model exhibited satisfactory agreement with experimental data. Lebbal et al. [106] introduced a comprehensive model that combines an electrochemical model with a dynamic thermal model. They used the nonlinear least squares method to identify unknown parameters of the electrochemical model, while thermal model parameters were estimated using first-order response properties. An observer was designed to diagnose the PEM system by generating residuals, enabling the detection and isolation of faults in sensors, actuators, and the system itself.

Understanding the phenomena on both sides of the MEA is crucial for comprehending flow dynamics within the PEM electrolysis cell. To express the different mass flows inside the cell, it is common to divide it into three primary sections the anode, the membrane, and the cathode, and subsequently calculate the mass flow for each species in each section. The overall mass conservation in a closed volume is expressed as (20):

$$\frac{dN}{dt} = \dot{N}_{\text{in}} - \dot{N}_{\text{out}} + \dot{N}_{\text{reac}} + \sum \dot{N}_{\text{diff}} \tag{20}$$

where $\dot{N}_{\text{in}}$ and $\dot{N}_{\text{out}}$ are the molar flows at the inlet and outlet of the electrolysis cell, $\dot{N}_{\text{reac}}$ is the molar flow of produced species, and $\sum \dot{N}_{\text{diff}}$ is the diffusive flux of species. Applying Faraday's law, the production rates of hydrogen and oxygen gases and water consumption are determined.

In water electrolysis, water transfer can occur from the anode to the cathode side or vice versa. Several authors have investigated detailed mass flow phenomena through the membrane, providing valuable insights into water flow dynamics in PEM electrolysis cells [107]. Water diffuses across the membrane due to three principal effects: Electro-osmotic drag, pressure-driven cross-flow, and diffusion driven by concentration gradients. Electro-osmotic drag is the dominant effect causing water permeation, driven by the transport of hydrated protons through the membrane from the anode to the cathode. The electro-osmotic drag coefficient n_d is empirical and depends on the membrane humidification [107] or on the temperature in the case of a fully hydrated membrane [108]. Multiple formulas exist in the literature to express n_d [108, 107, 109, 95]. Pressure-driven flow is caused by the pressure difference on both sides of the membrane (ΔP), allowing water to migrate from the cathode to the anode side. Darcy's law is commonly used to express this phenomenon [107, 104]. Diffusion driven by concentration gradients occurs due to the difference in water concentration on the anode and cathode sides and is expressed using Fick's law [110].

Calculating species concentration is a critical aspect of water electrolysis modeling, as it enables a comprehensive understanding and accurate prediction of water permeation from the anode to the cathode side. Moreover, concentration analysis plays a vital role in determining the partial pressures of each species inside the cell, which is necessary for calculating voltage losses due to diffusion in the electrochemical model. Various methods have been proposed in the literature for expressing the concentrations within the cell. In a study conducted by Marangio [70], Fick's laws were applied at the channel-electrode interface to determine particle concentrations on either side of the membrane. This method was subsequently employed in several other studies [104, 107, 2, 111]. Another widely used method for calculating concentration inside the cell is presented in [103, 107]. In these papers, the water concentrations on both sides of the membrane were represented as functions of membrane humidification; however, this method is limited to calculating the water concentration only and cannot be used to determine the concentrations of other species, such as oxygen and hydrogen.

Gas crossover is a crucial phenomenon observed in water electrolysis, where there is undesired movement of hydrogen to the anode side or, to a lesser extent, oxygen to the cathode side. This occurs due to the permeable nature of Nafion-type membranes, which allow gas permeation under various operational conditions. Gas crossover is a complex issue that can lead to mechanical degradation of the membrane and poses challenges in efficiently separating the two gases, oxygen and hydrogen [110]. Gas crossover in water electrolysis has been extensively studied in the literature. Mathematical models have been developed to address the impact of crossover on PEM performance and safety. Trinke et al. [112] investigated the effect of temperature and pressure on the permeation of hydrogen. They concluded that increases in pressure and temperature directly contribute to gas permeation, and this effect becomes more pronounced at high currents. Gas permeation occurs as a result of two major effects: convection and diffusion. Diffusion is caused by the random motion of gas molecules, while convection is driven by pressure gradients and electro-osmotic drag. Grigoriev et al. [113] proposed a model that describes gas crossover due to diffusion in high-pressure PEM electrolysis, adopting Fick's first law. In a subsequent study, Trinke et al. [114] observed that diffusion is the dominant mechanism for gas crossover in PEM water electrolysis, in contrast with alkaline water electrolysis. In the same paper, they proposed mathematical models for hydrogen crossover, estimating permeation due to diffusion using Fick's law, while convection was divided into permeation caused by pressure differences and electro-osmotic drag.

The electrochemical reaction in a PEM electrolysis is theoretically endothermic but becomes somewhat exothermic due to resistive losses and inefficiencies. Water is used to regulate the stack temperature, with the outlet temperature typically assumed equal to the water outlet temperature since water is continuously fed to the electrolysis in a loop. One of the simplest thermal models can be found in [115] and [74], where the outlet temperature is represented by a lumped equation involving the lumped thermal capacitance C_{th}, which is expressed using the density, volume, and specific heat of the electrolysis components [116]. However, obtaining these parameters can be difficult due to the lumped nature of the model and approximations made in the equations. This has led to the development of methods for determining the lumped capacitance through identification techniques or approximations [117, 116].

The total heat generated within the stack by the power supply is evaluated in conjunction with the heat losses incurred through radiation and convection. In PEM electrolysis, convection is associated with fluid flow over the cell surfaces; faster water flow promotes greater convective heat transfer, thereby influencing the thermal profile of the system [115]. Radiation losses, on the other hand, involve energy emission as electromagnetic waves due to thermal emission and depend on factors such as stack surface area A_s, ambient temperature T_{amb}.

4.2.2. Multi-Dimension model

The accuracy and reliability of a model depend on the validity of its underlying assumptions. Therefore, it is crucial to ensure that the assumptions made are realistic and representative of the real-world system being modeled. Multidimensional models that solve the conservation equations of mass, momentum, energy, species, and charge transport are commonly used to model and analyze the phenomena that happen inside the electrolysis accurately.

To simplify the modeling of PEM electrolysis, several common assumptions are often made, these include: ideal gas properties, ideal gas mixture, incompressible flow, laminar flow, isotropic and homogeneous membrane and electrode structures, zero ohmic potential drop in solid components [118, 119]. The choice of modeling approach ultimately depends on the specific application and the level of detail required for accurate system representation. Given the complexity of spatial models for PEM electrolysis cells, researchers often focus exclusively on the anode compartment, which is particularly prone to high overvoltages and instability.

One-Dimensional models One-dimensional (1D) models provide a simplistic representation of spatial variations in PEM electrolysis cells by considering transport mechanisms along a single axis, typically the axial direction of flow. These models assume uniform properties in the other two dimensions, making them computationally efficient and suitable for preliminary analyses.

For example, Han et al. [120] proposed a 1D model for the liquid-gas diffusion layer. In their model, Darcy's law was employed to express the momentum conservation of gas and liquid phases, while Leverett's function was used to represent capillary pressure, which depends on the contact angle between gas and liquid. Their study investigated the effects of different contact angles, porosity levels, and membrane thicknesses on PEM electrolysis performance, concluding that smaller contact angles, higher porosity, and reduced membrane thickness enhance cell performance. Huiyong Kim [95] developed a dynamic 1D model focusing on water transport and gas evaluation in PEM electrolysis. The partial differential equations (PDEs) were transformed into ordinary differential equations (ODEs) using the cubic spline collocation method (CSCM). However, this model was not experimentally validated. Recently, Shin et al. [121] presented a physics-based 1D dynamic model that accurately captured transient voltage responses, including overshoot and undershoot, with experimental validation (mean absolute error of 5.3 mV). Their results highlighted temperature as the dominant factor affecting stack performance, underscoring the importance of thermal management in dynamic PEM electrolysis.

Two-Dimensional models Two-dimensional (2D) models account for spatial variations in both the axial and radial directions, providing more detailed insights than 1D models. These models capture complex interactions between different components and phases within the PEM electrolysis cell.

Ojong et al. introduced a 2D model for the PTL [122]. Their study examined the effects of operating temperature, pressure, inlet water flow, PTL pore size, porosity, and thickness on PEM electrolysis performance. The Brinkmann equation was utilized to model the momentum transport of water, while Fick's law of diffusion described mass transport mechanisms within the PTL. The model demonstrated successful validation against experimental data across various operating conditions. Wrubel et al. developed a 2D model to describe multiphase transport in the liquid-gas diffusion layer (LGDL) containing highly structured pore arrays in PEM electrolysis cells [123]. Validated with recent data, their results indicated that larger pores improve water access to reaction areas and facilitate oxygen discharge, thereby enhancing membrane hydration. Hoseini Larimi et al. [97] constructed a 2D model for two-phase PEM electrolysis to investigate the effect of water velocity in the channels under two-phase flow regimes within the porous transport layer. The finite element method was employed to simulate the motion of the gas-liquid interface, providing valuable insights into bubble formation and detachment dynamics. Aubras et al. [124] developed a 2D mathematical model to evaluate heat and mass transfer, including bubble flow, at the anode of the PEM electrolysis. Their study suggested that bubble coalescence is associated with improved mass transfer and reduced ohmic resistance, thereby enhancing overall cell performance. Hu et al. [125] developed a 2D multiphysics model to analyze electrochemical processes in PEM electrolysis, focusing on how applied voltage and inlet flow rates influence performance. The study linked non-uniform distributions of temperature, current density, and water fraction to potential degradation risks such as hot spots and reactant starvation. Model validation against experiments showed that optimized operating conditions can yield an energy efficiency of up to 79 %, providing insights for future control and multi-objective optimization in microgrid applications.

Three-Dimensional models Three-dimensional (3D) models offer the highest level of detail by capturing spatial variations in all three dimensions, often represented by coordinates (x, y, z). These models provide comprehensive insights into transport mechanisms and interactions within PEM electrolysis cells but require significant computational resources.

One of the earliest 3D models was developed by Nie et al. [126, 127], focusing on flow within bipolar plates. In the second paper, the mixture model technique based on Navier-Stokes equations was introduced to describe two-phase flows on the anode side. The governing equations, including continuity, momentum, and energy equations, were solved using the finite volume scheme (FVS) and the SIMPLE algorithm. The numerical results showed good agreement with experimental data. Chen et al. [128] introduce a 3D model based on a new bipolar plate architecture with additional jet holes serving as outlets for generated gas and unreacted water flow. Simulated using COMSOL Multiphysics, the model revealed that jet holes improve polarization performance but adversely affect current distribution uniformity. Wang et al. [129] established a 3D non-isothermal, two-phase model for PEM electrolysis, incorporating conservation equations of mass, charge, momentum, and energy. Utilizing the PARDISO solver within COMSOL Multiphysics, their study investigated the effects of inlet water velocity, inlet water temperature, contact angle, and porosity on PEM electrolysis performance. Jiang et al. [118] developed a comprehensive 3D model accounting for hydrogen crossover to the anode side, simulated using ANSYS FLUENT. The model showed good agreement with experimental data and demonstrated that two-phase models are more accurate than single-phase models. It was reported that low water flow rates increase gas accumulation in channels, thereby decreasing cell performance. Li et al.[130] developed a fully validated 3D multiphysics model to resolve mass transport and current distribution in PEM electrolysis cells. The model demonstrated that non-uniform water saturation and current density arise from strong interactions among bipolar plates, PTLs, and membrane thickness. Wide lands in anode bipolar plates were shown to block PTL pores, leading to local dehydration and current density drops, which could be mitigated by reducing land width or adopting flow-enhanced diffusion layers. Furthermore, while thinner membranes improve performance, they exacerbate non-uniform water and current distribution, risking local dry-out and current crowding. This work highlights the importance of spatially resolved models to guide component design and integration in PEM electrolysis.

4.3. Degradation modeling

Incorporating degradation mechanisms into modeling PEM electrolysis is crucial for predicting long-term performance and enhancing system reliability. While the previous sections have detailed the fundamental components and degradation processes affecting PEM electrolysis, integrating these insights into comprehensive models remains a significant challenge. Accurate degradation modeling bridges the understanding of material degradation (discussed previously) with the development of effective diagnostic and control strategies (to be explored subsequently). In particular, operational conditions such as temperature, current density, and water management profoundly influence the lifetime of the PEM electrolysis and thus should be modeled properly. However, comprehensive degradation models specifically tailored for PEM electrolysis remain scarce in the literature. Chandesris et al. [131] addressed this gap by developing a one-dimensional model incorporating chemical membrane degradation to examine the effects of temperature and current density on membrane thinning. Similarly, Norazahar et al. [132] presented a reliability model focusing on variables such as membrane drying and hot spot formation, emphasizing the importance of controlling current density and maintaining adequate water quantity at the anode to ensure operational safety and reliability. Dominguez et al. [133] apply a temporal multiscale method to simulate degradation at the system level by coupling fast-scale reaction/transport with slow-scale catalyst dissolution phenomena, significantly reducing computational cost. A recent study developed a multi-physics coupling model linking electrochemical reactions, gas crossover, and membrane degradation to evaluate the role of membrane thickness in PEM electrolysis [134], the model helps to identify the optimal membrane thickness for each operation condition.

Given the similarities in some degradation mechanisms between PEM fuel cells and PEM electrolysis, it is advantageous to utilize existing modeling approaches and degradation models developed for PEM fuel cells to study electrolysis degradation, as degradation modeling in PEM fuel cells is relatively more advanced [135]. Both systems exhibit common degradation phenomena, such as catalyst dissolution resulting from fluctuation current (e.g., platinum on the cathode side) and membrane thinning caused by crossover (e.g., Nafion), resulting from similar electrochemical processes and material properties.

These models underscore the vital role of degradation modeling in optimizing operational strategies and enhancing the longevity of PEM electrolysis. By accurately predicting degradation behavior under various operating conditions, such models enable the development of control strategies that mitigate degradation effects, improve system reliability, and ensure sustainable hydrogen production.

4.4. Discussion on modeling approaches and limitations

Zero-dimensional models simplify the PEM electrolysis as a lumped system without spatial variations. They are computationally efficient and useful for system-level analyses and control design. However, their inability to capture spatial distributions of the modeled variables limits their accuracy in representing localized phenomena such as concentration distribution or temperature hotspots. Additionally, the neglect of heat transfer and pressure effects, as seen in some studies [103], may lead to oversimplified predictions that do not fully align with experimental observations. In both PEM electrolysis and fuel cell modeling, three-dimensional (3D) models offer potentially the most accurate simulations of transport mechanisms by capturing spatial variations across all three dimensions (x, y, z). This comprehensive approach enables a detailed understanding of mass, momentum, energy, species, and charge transport phenomena, which is essential for optimizing system performance and enhancing efficiency and durability [94]. However, the complexity of model parameter identification and the significant computational resources required for 3D models are notable drawbacks compared to one-dimensional (1D) and two-dimensional (2D) models, which remain favored for their simplicity and lower computational demands. A common challenge across all modeling approaches is the accurate representation of multiphase flow, especially the dynamics of gas bubble formation, growth, coalescence, and detachment within the cell. Gas bubbles affect mass transport by blocking active sites and altering local flow fields, leading to increased overpotentials and decreased cell efficiency. While methods like the Volume of Fluid (VOF) [98, 136] and mixture models [137, 99] have been employed to simulate two-phase flows, capturing the intricate interactions between phases remains complex and computationally intensive.

Another limitation is the lack of models that incorporate degradation mechanisms over time, such as catalyst dissolution, membrane thinning, or component aging. Most existing models focus on initial performance and do not account for the gradual changes during prolonged operation. Incorporating degradation kinetics into models is essential for predicting long-term performance, planning maintenance, and improving durability. Given these limitations, there is a clear need to develop models that balance accuracy with computational efficiency. Simplified models that can capture essential dynamics without excessive computational demands would be highly beneficial, particularly for control system design and real-time optimization. Additionally, integrating degradation processes into existing models would enhance their predictive capabilities regarding component lifespan and system reliability.

Emerging modeling techniques, such as Physics-Informed Neural Networks (PINNs), offer promising avenues for addressing the aforementioned challenges that lie in both model development and resolution. PINNs can integrate physical laws with experimental data to provide accurate and computationally efficient simulations [138]. PINNs have the potential to capture complex flow behaviors and underlying physics more effectively than traditional methods [139]. Moreover, the PINN approach embeds complex PDE solutions in multi-layer neural networks whose implementation complexity could be much more reduced compared to classical numerical methods such as finite element methods [140].

In summary, while significant progress has been made in modeling PEM electrolysis systems, gaps remain that require further research. Advancements in modeling multiphase flows, incorporating degradation mechanisms, and developing computationally efficient models are essential for optimizing PEM electrolysis. Addressing these challenges is essential for achieving optimal operation, as they enable predictive control and performance optimization under real conditions, leading to more efficient, durable, and reliable systems.

Insights from modeling efforts can not only enhance the understanding of PEM electrolysis behavior but also provide the basis for the development of effective diagnostic tools, as illustrated in Fig. 2. By identifying key parameters and potential issues through modeling, specific diagnostic methods to monitor critical performance criteria can be tailored at different levels of an electrolysis system. This progression leads us to focus on diagnostics, where they play a pivotal role in penetrating and validating models, as well as providing real-time feedback on system operation.

5. Diagnostic Methods for Optimal Operation of PEM Electrolysis

Diagnostics are indispensable for achieving optimal operation, as they allow real-time monitoring of PEM electrolysis performance and health. Diagnostic tools facilitate a deeper understanding of multiphysics processes, allow the detection of degradation mechanisms, and guide improvements in system design and operation. These techniques are broadly categorized into *in-situ* (including *in-operando*) and *ex-situ* methods. *In-situ* diagnostics involve measurements performed on the operating electrolysis without disassembling it, allowing real-time monitoring under actual operating conditions. *In-operando* diagnostics are a subset of *in-situ* methods conducted under dynamic operating conditions, capturing the system's behavior in its authentic environment [141]. Conversely, *ex-situ* diagnostics involve analyzing components outside their operational context, often after disassembly, to gain detailed insights into their physical and chemical properties [141]. While *ex-situ* methods provide comprehensive insights, they cannot capture transient phenomena occurring during actual operation.

This section reviews electrochemical, physical, and software-based diagnostic techniques employed in diagnosing PEMWE performance and degradation, highlighting their principles, applications, and contributions to advancing PEM electrolysis technology.

5.1. Electrochemical Characterization

Electrochemical characterization techniques are pivotal for elucidating the fundamental processes within PEMWEs and assessing their performance under operational conditions. These methods provide insights into kinetics, mass transport, and ohmic losses, which are essential for optimizing cell design and operation.

Among the various techniques, polarization curves are one of the most prevalent *in-situ* methods for characterizing the performance of electrolysis and fuel cells. They depict the relationship between cell voltage and current density, serving as a direct indicator of cell efficiency and performance [11, 142]. Polarization curves can be generated using potentiostatic methods, where the voltage is controlled and the resulting current is measured, or galvanostatic methods, where the current is controlled and the voltage response is recorded. A typical polarization curve exhibits distinct regions corresponding to activation overpotentials, ohmic losses, and mass transport limitations. At low current densities, activation overpotentials dominate due to the sluggish kinetics of the electrochemical reactions, particularly the OER at the anode. In the intermediate current density region, ohmic losses, primarily due to ionic resistance in the membrane and electronic resistance in cell components, become significant. At high current densities, mass transport limitations and phenomena such as gas bubble formation lead to additional voltage increases [143]. While polarization curves are effective for assessing overall cell performance and identifying deviations from expected behavior, they do not distinguish between different sources of losses or pinpoint specific degradation mechanisms [144].

Electrochemical Impedance Spectroscopy (EIS) is a powerful *in-situ* diagnostic tool that provides frequency-dependent information about the electrochemical processes occurring within the PEM electrolysis [145]. In EIS, a small-amplitude sinusoidal voltage or current perturbation is applied over a range of frequencies, typically from 1 mHz to 100 kHz, and the resulting current or voltage response is measured. The impedance spectrum obtained contains valuable information about various resistive and capacitive elements within the cell, such as charge transfer resistance, double-layer capacitance, and mass transport resistance.

Data from EIS are often represented in Nyquist or Bode plots, which allow for the differentiation of processes occurring at different time scales. High frequencies reflect ohmic resistances primarily due to ionic resistance in the membrane and electronic resistance in cell components. Intermediate frequencies are associated with charge transfer resistance and double-layer capacitance, relating to electrochemical reaction kinetics at the electrode interfaces. Low frequencies represent mass transport limitations, such as the diffusion of reactants and removal of products in the porous layers and membrane [146, 147]. For instance, Van der Steeg et al. [142] demonstrated how EIS could distinguish

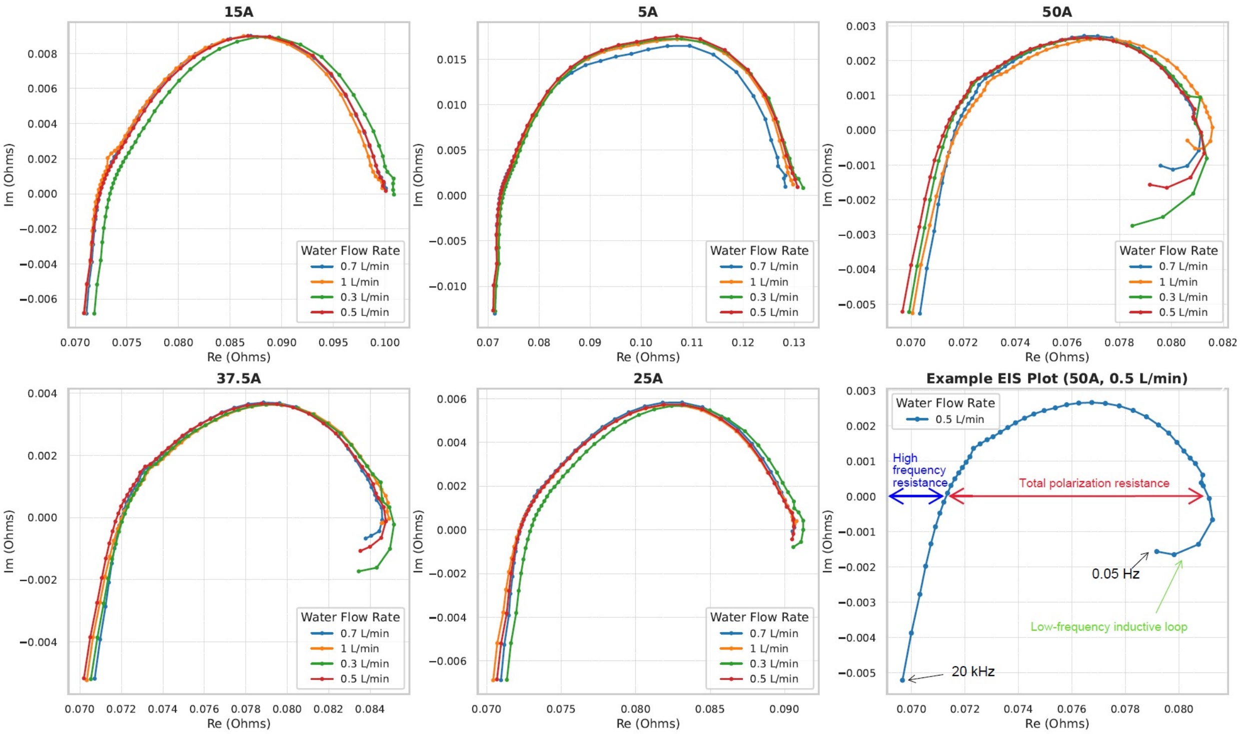


Figure 8: EIS results for a 10-cell under varying water flow rates (0.3–1L/min) and current densities (5–50 A)

between different loss mechanisms in PEMWEs. They showed that increasing membrane thickness led to higher ohmic resistance, observable as a horizontal shift in the Nyquist plot. Temperature variations affected activation losses, changing the size of the semicircle corresponding to charge transfer resistance.

Researchers often model the impedance data using Electrical Equivalent Circuits (EECs) to quantify the resistive and capacitive elements within the cell [148, 142], which is also known as model-based modeling techniques. Other researchers tend to quantify the results from the EIS using free modeling techniques such as the distribution of relaxation times [149, 150, 151]. An available MATLAB GUI toolbox has also been developed to facilitate the solution of DRT regularization problems [**?**].

Since water flow diagnostics using EIS is relatively rare in the literature, we conducted several experiments to illustrate the effect of water flow rates on EIS measurements in PEM electrolysis. Fig. 8 presents an example of EIS results obtained from experiments on a 10-cell. The stack was operated at currents up to 50 A and water flow rates ranging from 0.3 to 1 L/min. EIS measurements were conducted at five different current densities (5 A, 15 A, 25 A, 37.5 A, and 50 A) and four water flow rates (0.3 L/min, 0.5 L/min, 0.7 L/min, and 1 L/min) for each current density. During the EIS measurements, the amplitude of the AC perturbation was set to 10 % of the DC supply current, covering a frequency range from 50 mHz to 20 kHz. The Nyquist plot illustrates how different frequencies correspond to distinct loss mechanisms within the electrolysis. The high-frequency intercept on the real axis represents the ohmic resistance. The semicircle at intermediate frequencies corresponds to the charge transfer resistance and double-layer capacitance. The tail at low frequencies highlights mass transport limitations, which can be influenced by factors such as water flow rates and gas bubble accumulation. The results demonstrate the effect of different water flow rates on stack performance. Specifically, water flow consistently affects the low-frequency region, particularly the inductive loop. An increase in the water flow rate leads to a decrease in the inductive loop at high currents, such as 37.5 A and 50 A. This reduction occurs because higher water flow rates enhance mass transport by promoting the removal of gas bubbles and improving reactant delivery, thereby decreasing mass transport resistance at high currents.

Cyclic Voltammetry (CV) is another *in-situ* technique used to investigate the electrochemical properties of catalyst layers, particularly the Electrochemically Active Surface Area (ECSA), and to gain insights into kinetics, surface properties, and reaction mechanisms occurring at the electrodes [152]. In CV, the potential of the working electrode

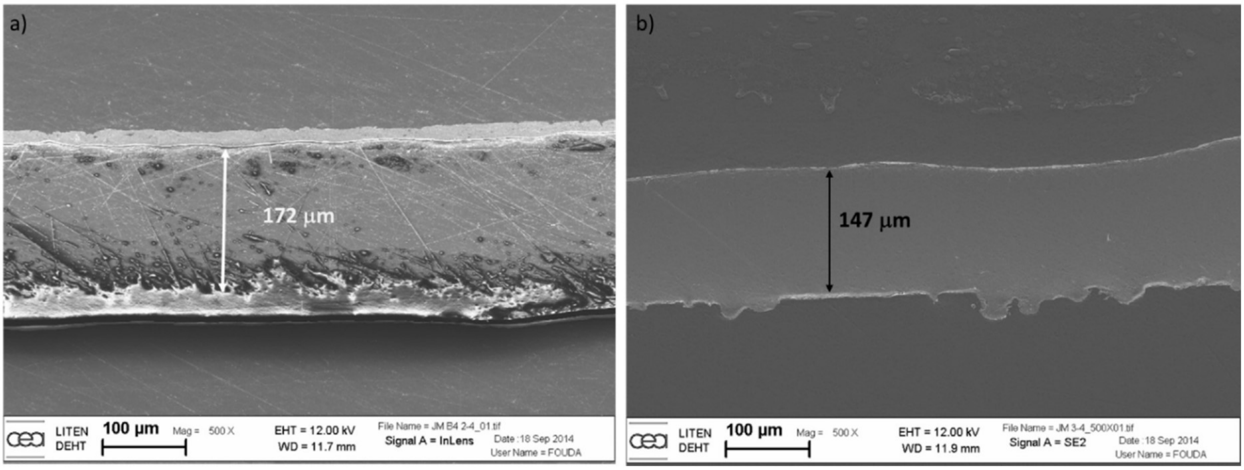


Figure 9: Cross-sectional SEM images of membranes. (a) Fresh membrane after conditioning, (b) Aged membrane operated at 80 °C for 1440 hours. [39]

is cyclically swept between two limit values at a specified scan rate, and the resulting current is recorded. Peaks in the cyclic voltammogram correspond to the redox processes of the catalyst material. CV is valuable for determining the ECSA by measuring the charge associated with specific adsorption processes, for instance, the hydrogen adsorption charge is widely accepted as 210 μCcm^{-2} for platinum [153]. Iridium catalysts' determination is more complex due to varying pseudocapacitive charges, with reported values ranging from 90 to 596μC cm^{-2} [154]. Careful selection of the potential window is essential to avoid excessive potential changes that can lead to catalyst degradation and measurement artifacts when determining the ECSA.

5.2. Physical Characterization

Physical characterization techniques are essential for diagnosing degradation mechanisms by identifying changes in the physical structure, composition, and morphology of PEMWE components during or after operation. High-resolution imaging and analytical methods are required due to the nanoscale features of materials used in the electrolysis.

Scanning Electron Microscopy (SEM) utilizes a focused beam of electrons to scan the surface of a specimen, producing high-resolution images that reveal surface morphology and topography [11]. SEM is extensively used in PEMWE research for examining the surface morphology of catalysts and PTLs, identifying degradation features such as cracks, pinholes, or thinning in membranes, detecting particle agglomeration or sintering of catalyst nanoparticles [155], and observing surface contamination or deposition of impurities [156]. Fig. 9 presents cross-sectional SEM images of a fresh membrane and an aged membrane operated at 80°C for 1440 hours. The thickness of the aged membrane is significantly reduced compared to the fresh one. While SEM provides detailed surface information, it does not reveal internal structures or compositions beneath the surface layer.

Transmission Electron Microscopy (TEM) involves transmitting a beam of electrons through an ultra-thin specimen, providing images with atomic or near-atomic resolution [11]. TEM is used to analyze the internal microstructure and crystallography of catalyst particles, observe lattice fringes, defects, and grain boundaries, and investigate catalyst degradation mechanisms such as dissolution or particle growth [40]. TEM requires complex sample preparation and is typically used for detailed analysis of small specimen areas.

X-ray Diffraction (XRD) is a non-destructive technique used to determine the crystalline structure, phase composition, and crystallite size of materials [11]. In PEMWE research, XRD is employed to identify phases and compounds present in catalysts and other components, detect changes in crystallinity or phase transitions due to operational stresses, and measure particle sizes and strain within the crystal lattice [48]. XRD complements electron microscopy by providing bulk structural information. Altus et al. [157] demonstrated that combining neutron and X-ray imaging offers complementary diagnostic capabilities in PEM electrolysis: neutron imaging is sensitive to water/gas phases and transport, while X-ray reveals structural changes. This dual imaging approach allows internal flow phenomena and component degradation to be visualized in situ. Lee et al. [158] employed full-field transmission X-ray microscopy (30 nm resolution) to visualize nanoscale pore structures in Ir-based catalyst layers. They showed that while most pores were <200 nm, larger macropores governed gas removal, linking morphology directly to transport and utilization. This highlights the value of high-resolution X-ray diagnostics for understanding catalyst-layer performance.

Additional analytical techniques that have been used for fuel cells can provide valuable insights into material properties and degradation phenomena. X-ray Photoelectron Spectroscopy (XPS) provides information on the elemental composition and chemical state of surfaces, which is useful for analyzing catalyst oxidation states and surface contamination [159]. Atomic Force Microscopy (AFM) offers topographical mapping at the nanoscale, enabling the measurement of surface roughness and detecting nanoscale defects [160]. Fourier Transform Infrared Spectroscopy (FTIR) is used to identify chemical bonds and functional groups, aiding in the analysis of membrane degradation and contamination [161].

Another interesting physical diagnostic technique that can be used is flow visualization, which can complement the electrochemical methods by enabling the direct observation of fluid dynamics and two-phase flow within the cell. Using optically transparent cell components and high-speed imaging, researchers can study bubble nucleation and growth, bubble detachment and transport, and flow patterns within the cell [162, 163]. These observations are critical for improving cell design by optimizing flow field geometries to enhance gas removal and water distribution. Understanding bubble dynamics is essential for reducing mass transport limitations caused by bubble accumulation, which can block active sites and increase resistance. Additionally, flow visualization aids in enhancing modeling accuracy by providing empirical data to validate computational fluid dynamics (CFD) simulations [164, 165].

5.3. Software-Based Diagnostic Methods

Beyond traditional electrochemical and physical characterization techniques, software sensors and observers have emerged as powerful tools for diagnosing and optimizing PEM electrolysis systems. These methods use mathematical models and algorithms to estimate internal states and parameters that are not directly measurable during operation.

Software sensors, also known as virtual sensors or observers, leverage available measurements and system models to infer quantities within the system that are otherwise unmeasurable. They are particularly valuable for estimating degradation-related parameters such as bubble coverage, changes in catalyst geometry, and membrane thinning. By providing real-time estimations of these internal states, software sensors enhance the diagnostic capabilities of the system without the need for additional hardware, thereby reducing system costs and complexity while eliminating potential points of failure associated with physical sensors. This real-time monitoring enables prompt detection of faults and facilitates corrective actions to mitigate degradation.

Implementing software-based diagnostics in PEM electrolysis systems involves developing accurate mathematical models that capture the dynamic behavior of the PEMWE. Observer filters are designed to estimate internal states based on these models and the available measurements. Common observer designs include Kalman filters, which are effective for systems with stochastic noise and provide estimates by minimizing the error covariance; Luenberger observers, suitable for deterministic systems and offering a straightforward approach for state estimation; and nonlinear observers, designed to handle the inherent nonlinear dynamics of the processes [166]. Despite their advantages, the effectiveness of software sensors depends on several factors. The reliability of state estimations hinges on the accuracy of the system model, inaccurate models can lead to erroneous estimations, potentially compromising system safety and efficiency. Real-time estimation requires efficient algorithms capable of rapid data processing, which may necessitate advanced computational resources or simplification of models. Additionally, measurement noise from physical sensors used as inputs may affect the observer's performance, necessitating robust filtering and noise attenuation techniques.

Software sensors not only enhance diagnostics but also integrate seamlessly with control strategies. They provide feedback for high-level control, where estimated states inform controllers about degradation trends, enabling strategic adjustments to operating conditions for degradation mitigation. At the low-level control, they support precise maintenance of optimal operating parameters, improving overall system responsiveness. Fig. 10 illustrates the integration of software sensors and observers within a PEM electrolysis system

5.4. Discussion of Diagnostic Methods

Combining multiple diagnostic methods provides a comprehensive picture of PEMWE performance and health, bridging electrochemical signals with physical and structural changes. Electrochemical techniques such as EIS and CV detect evolving performance losses, while imaging tools like SEM or TEM reveal the material-level mechanisms behind them, and flow visualization uncovers hidden transport issues. When integrated, these diagnostics not only

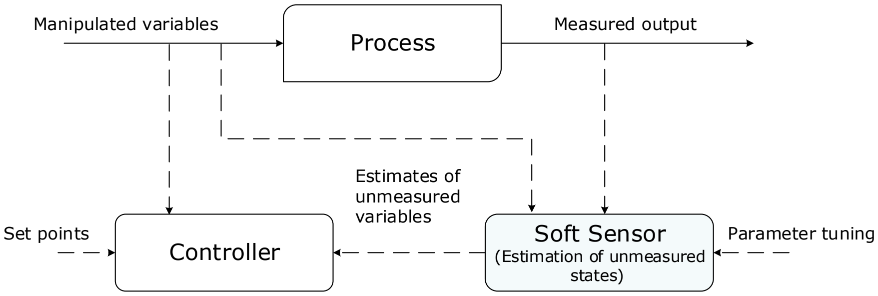


Figure 10: Integration of Software Sensors and Observers in a PEM Electrolysis System

identify root causes of degradation-such as catalyst dissolution, membrane thinning, or PTL corrosion-but also enable early detection of failures in real time. In practical terms, this contributes to optimal operation by guiding adaptive control and targeted maintenance: diagnostic insights allow timely adjustments to temperature, flow, or current density that preserve efficiency and slow degradation. As diagnostic technologies advance, they will further strengthen the ability to sustain high efficiency, durability, and reliability in PEM electrolysis.

Building upon the insights gained from diagnostics and modeling, we now focus on the implementation of control strategies, the final component of our Integrated Optimization Framework (Fig. 2). Effective control is crucial for managing the complex and dynamic processes within PEM electrolysis systems, ensuring optimal performance while mitigating degradation. By leveraging detailed models and real-time diagnostic data, control strategies can proactively adjust operational parameters, enhancing efficiency and extending system lifespan. This section outlines the primary control objectives in PEM electrolysis and explores specific techniques used to achieve these goals, emphasizing how they integrate with the other elements of the framework to optimize system operation.

6. Control strategies

Effective control strategies are pivotal for managing the complex and dynamic processes within PEM electrolysis systems. By leveraging insights from modeling and diagnostics, the optimal operation is finally achieved by the specifically designed control strategy. After clarifying the operation objectives and some industrial operation cases, this section discusses primary control objectives, reviews various control techniques, and demonstrates how they are applied in PEM electrolysis.

6.1. Operation objectives and industrial operational strategies

Depending on the objectives desired by the PEMWE operators, the optimal operation of PEMWE systems refers to one or some of the following aspects: efficiency optimization, hydrogen production rate tracking, durability management, safety assurance, and grid service participation. Nowadays, the operation objectives of industrial PEMWE systems are focused on the hydrogen production and grid service participation aspects and they are often realized through high-level system design and sizing with simple control designs.

Large systems rely on multistack architectures to meet variable hydrogen demand. Instead of one very large stack, several stacks are grouped in parallel, allowing individual modules to be throttled or taken offline for maintenance. For example, Iberdrola's Puertollano facility is a 20 MW PEM plant composed of 16 stacks of 1.25 MW each [188]. Fully parallel designs, where each stack has dedicated rectifiers, pumps, and gas separators, provide maximum flexibility but increase capital cost. More integrated clusters share power or water circuits, lowering cost but limiting independent control [189]. This trade-off between flexibility and cost must be reflected in realistic scheduling and optimization models.

The Puertollano project in Spain couples a 20 MW PEM system with wind and solar power, producing around 360 kg H_2 per hour (3,000 t/year). A 20 MWh battery buffer smooths renewable fluctuations and ensures stable hydrogen flow to downstream ammonia synthesis [188]. By contrast, the REFHYNE project in Germany integrates a 10 MW PEM electrolysis directly into Shell's Rhineland refinery [193]. Operating mainly as a baseload source, it supplies about 1,300 t H_2/year for hydrodesulfurization. Its direct link to the refinery hydrogen grid required strict control of purity, pressure, and reliability. Building on its success, REFHYNE II was launched in 2024 and is scheduled

Table 4
Relations between control and operation in PEMWE systems

Operational aspect	Control component implication	Control objective
Hydrogen production rate tracking	Power conditioning and energy management	Power repartition and fast dynamic control to track power fluctuations
Efficiency optimization	Temperature, pressure and water flow rate static and dynamic regulation	Trade-off between efficiency and response speed
Degradation minimization	Power conditioning; Temperature, pressure and water flow rate static and dynamic regulation	Optimize power, pressure, temperature and water flow rate values and transitions to mitigate performance degradations; Balance uniformity across cells and prevent hot spots
Start-up/shut-down sequences	Power converter, valves, pumps of water and gas lines	Ensures safe power, thermal and gas/water management during transients
Grid services	Power modulation of single/multiple stacks and electrolyzer modules	High-level energy management to achieve required demand response
Hydrogen quality and purity	Purge, pressure, temperature and flow rate regulation; purificator control	Satisfy safety and compliance standards

to begin operation in 2027, scaling capacity to 100 MW. Together, these projects illustrate how different industrial contexts-renewable-driven flexibility versus refinery baseload integration-shape the strategies for achieving optimal PEM operation.

While various designs have been applied in different industrial systems, the control strategies dedicated to optimal operations are still rarely reported. As shown in Table 4, a dedicated control strategy is important to achieve different operation objectives.

6.2. Control objectives

PEM electrolysis systems are inherently complex dynamical systems characterized by multiple inputs and outputs. They are highly sensitive to variations in operational conditions such as power supply fluctuations, inlet water flow rates, operating temperatures, and system pressures. These operating conditions substantially influence both electrochemical efficiency and material durability. The principal objectives in PEM electrolysis involve maintaining stable current densities, regulating temperature, managing water flow, and optimizing pressure.

Stabilizing current density and power input is crucial for ensuring consistent hydrogen production and minimizing the degradation of system components. Achieving stable current densities despite fluctuations in power input poses a particular challenge, especially when the PEMWE is integrated with renewable energy sources like solar or wind power plants, which are inherently intermittent [167]. Consistent current density ensures uniform electrochemical reactions within the cell, reducing stress on PEMWE components and thereby extending their operational life. To harness the potential of renewable energy while maintaining current stability, energy storage units are often installed to smooth current variations [168, 169, 170]. Additionally, energy management strategies must be designed to handle current transients effectively, necessitating controllers that are robust and capable of quickly addressing nonlinearities and rapid transitions.

Regulating the operating temperature is vital for balancing reaction kinetics and system efficiency. Precise thermal management enhances electrochemical reaction rates, minimizes voltage losses, and curtails material degradation by averting overheating [112]. Precise temperature control contributes to improved efficiency and prolongs the lifespan of the PEMWE by preventing overheating and associated material degradation. Since stack temperature influences nearly every aspect of the polarization curve, including hydrogen crossover rates, maintaining an optimal thermal environment is essential for both performance and safety. Temperature regulation can be achieved through the heat exchanger [171].

Managing water flow and membrane hydration further safeguards PEMWE stability by preventing inadequate hydration (leading to performance losses) and excessive flooding [115]. The water flowing through the PEMWE can removes heat from the system and allows for the regulation of the temperature gradient between the inlet and outlet by adjusting the flow rate. Additionally, ensuring sufficient water flow is crucial for accessing reaction sites, effectively removing the gases produced during electrolysis, and controlling bubble coverage within the PEMWE. Optimizing water flow rates can further enhance hydrogen production and reduce water and energy consumption, which is particularly important in environments where water resources are limited or costly to procure.

Optimizing pressure levels on both the anode and cathode sides enhances gas separation efficiency and minimizes gas crossover between the anode and cathode compartments. By regulating system pressure, safe and efficient operation could be ensured, and the purity of the produced hydrogen could be maintained more easily. Appropriate pressure control also reduces mechanical stress on system components, contributing to overall durability.

6.3. Control Techniques

A diverse range of control strategies has been developed and implemented to achieve the operational objectives of PEM electrolysis systems. Table 5 provides a comprehensive summary of these control methods along with their corresponding goals as documented in the literature. These strategies span from conventional linear controllers to nonlinear and adaptive controllers, each specifically designed to address the unique challenges associated with PEM electrolysis.

Table 5: Summary of Control Techniques, Objectives, and Systems Controlled in PEM Electrolysis Systems

Reference	**Control Technique**	**Control oblectives**	**Results and major contributions**
Maamouri et al. [173]	PID Controller	Stabilizing current density and power input	Demonstrated that controlling the current using a PID controller yields better hydrogen production consistency than voltage control.
Guilbert et al. [174]	PID Controller	Stabilizing current density and power input	Proposed a methodology for designing PID controllers for stacked interleaved DC-DC buck converters, finding that current control configurations outperform voltage control in small-scale, high-current, low-voltage systems.
Dang et al. [175]	PID Controller	Regulating the operating temperature	Developed and experimentally validated a PID controller to regulate the operating temperature of a .
Keller et al. [176]	Adaptive PID Controller	Regulating the operating temperature	Implemented an adaptive PID controller in a 100 kW system integrated with photovoltaic and wind energy profiles, providing faster response times and reduced overshoot, ensuring consistent temperature regulation despite fluctuating input conditions.
Garrigos et al. [177]	PI Controller	Stabilizing current density and power input	Implemented a PI controller for the inner current control loop of a DC-DC converter to track reference signals faster and eliminate steady-state errors.
Guida et al. [178]	Gain-Scheduled PI Controller	Stabilizing current density and power input	Gain-scheduled the proportional gain of a PI controller to control the stack current with consistent dynamic performance across all operating points, addressing variability in input voltage from renewable energy sources.
Guilbert et al. [179]	Indirect SMC	Stabilizing current density and power input	Implemented indirect SMC for manipulating the duty cycle of the pulse-width modulator in a DC-DC converter, effectively controlling the PEMWE stack current.
Yodwong et al. [180]	Improved SMC Controller	Stabilizing current density and power input	Introduced an Improved SMC for a three-level interleaved buck converter (TLIBC) used in a PEM electrolysis supplied by renewable energy sources. Experimental results confirmed that the proposed controller effectively manages input power variations, achieving faster response times and maintaining stable hydrogen production rates even under fluctuating operational conditions.

Continued on next page

Ogumerem et al. [181]	Model Predictive Control (MPC)	Managing water flow, Regulating the operating temperature	Implemented MPC to regulate water flow, thereby controlling the temperature difference between the inlet and outlet of the PEMWE. This strategy effectively maintained the temperature within a predefined safe range, enhancing system stability and performance.
Flamm et al. [182]	MPC with Piece-Wise Affine Approximations	Stabilizing current density and power input	Used piece-wise affine approximations within an MPC framework to reduce computational requirements while achieving optimal hydrogen production from a combination of photovoltaic and grid power supplies.
Zhao et al. [183]	Neural Networks Integrated with MPC	Stabilizing current density and power input	Integrated neural networks with MPC to model PEMWE systems, significantly reducing computational costs and improving performance compared to adaptive PID controllers.
Tabanjat et al. [184]	Fuzzy Logic Control	Regulating the operating temperature, Stabilizing current density and power input	Utilized fuzzy logic to dynamically adjust temperature setpoints based on real-time hydrogen production rates, enhancing the robustness and flexibility of temperature control under variable operational demands.
Cano et al. [185]	Fuzzy Logic Control	Stabilizing current density and power input	Used fuzzy logic to generate power input references for both an PEMWE and a fuel cell in a hybrid renewable energy system, effectively minimizing start-stops and reducing system degradation.
Dahbi et al. [172]	Feedforward Control	Managing water flow	Implemented a feedforward control algorithm for the feedwater flow rate, optimizing hydrogen production rate and stack efficiency. By deriving an optimal flow rate value based on system parameters, they improved overall system performance without the need for feedback measurements.
Sankar et al. [186]	Nonlinear Control Algorithms (SMC)	Stabilizing current density and power input, Regulating the operating temperature	Implemented SMC for controlling a PEM fuel cell coupled to a water PEMWE, demonstrating enhanced power production regulation and hydrogen production referencing through coordinated control of stack current and temperature.
Ayubirad et al. [187]	PI controller	Maintain pressure constraints during dynamic power changes	Developed a control-oriented model capturing pressure/flow dynamics and a governor to prevent pressure violations while maximizing hydrogen output. Effective in simulations compared to simple filtering.

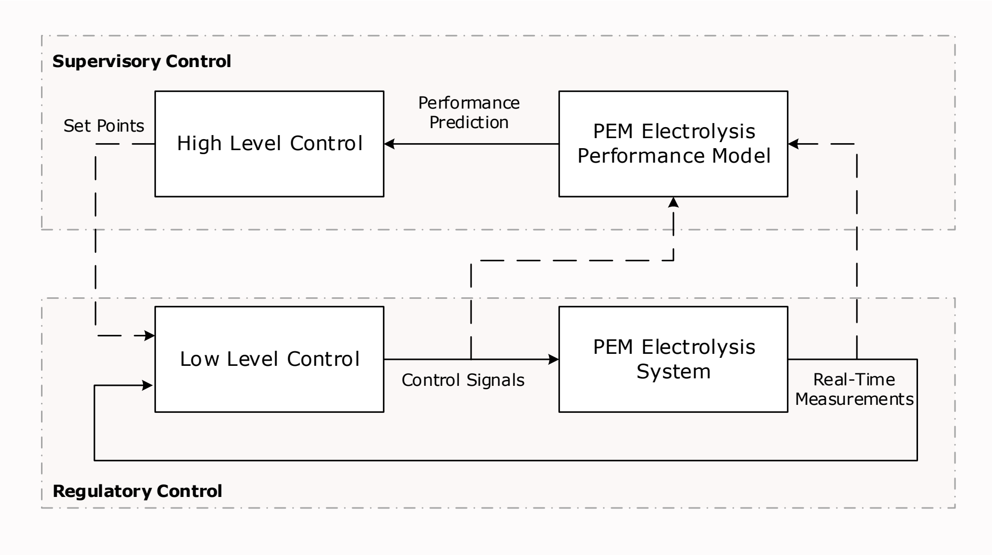


Figure 11: Hierarchical Control Architecture for PEM Electrolysis Systems

6.4. Discussion on PEMWE system control design

Ultimately, effective control is what translates insights from materials, degradation, modeling, and diagnostics into practice, ensuring PEM electrolysis consistently operate at their optimal point. Building on insights from our integrated optimization framework, the control design can be synthesized in a hierarchical structure, encompassing two layers: Supervisory Control and Regulatory Control, as can be seen in Fig. 11. This hierarchical structure ensures comprehensive control over the system by integrating various control strategies to address both high-level optimization and real-time operational adjustments.

The Supervisory Control Layer focuses on strategic system management, determining optimal setpoints for critical parameters such as current density, temperature, water flow, and pressure. It leverages the insights gained from modeling and diagnostics to enhance operational efficiency and minimize degradation. This layer ensures that the system operates within the optimal conditions defined by the model-based predictions, adapting to changes based on diagnostic feedback.

The Regulatory Control Layer provides real-time control to maintain these setpoints, ensuring stability and quick response to any operational disturbances. This layer incorporates PID controllers, SMC, MPC, and other advanced techniques, ensuring precise regulation of system parameters. The Regulatory Layer plays a crucial role in implementing the setpoints provided by the Supervisory Layer and mitigating any deviations caused by system dynamics or external fluctuations. It should be noted that most control methods proposed in Table 5 belong to this layer.

The selection of appropriate control strategies is critical for achieving the control objectives in PEM electrolysis systems. Traditional controllers like PID are simple and widely used, but advanced control methods like SMC, MPC, and fuzzy logic offer enhanced performance in handling system nonlinearities and intermittencies. The effectiveness of each control technique depends on the specific system configuration, operational conditions, and integration with renewable energy sources. Continuous advancements in control methodologies contribute significantly to enhancing the performance, efficiency, and durability of PEM electrolysis. By adopting a hierarchical control architecture and leveraging advanced control techniques, it is promising for PEM electrolysis systems to achieve optimal operation, adapt to variable conditions, and mitigate degradation mechanisms.

7. Prospects

To ensure optimal operation of PEM electrolysis, multi-objective optimization techniques are essential. Building on the integrated optimization framework outlined in this review, several critical avenues of research emerge to advance PEM water electrolysis toward its full potential.

- At the component level, a deeper understanding of material degradation remains paramount, as key failure mechanisms are not yet fully clarified under realistic operating conditions. Moreover, it is still uncertain whether steady high-current operation or dynamic load cycling exerts a stronger influence on long-term durability. In addition, long-term studies of PEM electrolysis under realistic PV or wind profiles are scarce, despite their importance for providing critical insights into system operation and durability. The literature highlights a clear need for additional AST protocols that define specific stressors and adopt standardized durability metrics.

- High-fidelity multiphysics models must be developed to capture the complex, coupled phenomena in PEMWE cells and their internal interactions and those with other system components. Particular attention should be paid to the effects of bubble dynamics and gas crossover which have not yet been completely understood and modeled. Future models must span multiple scales (from microstructure to full stack). Such models, potentially enhanced by data-driven or AI techniques, can provide valuable insights into performance-limiting processes and guide the design and operations of next-generation PEMWE. The literature reveals a clear gap in electrolysis degradation models, where robustness and generalizability should be considered critical criteria in their development. Despite significant progress in modeling techniques, especially data-driven methods, literature on PEM electrolysis reveals a clear lack in open-source data availability. Such data are crucial for both training and validating these models.

- Diagnostics must also advance in tandem. Real-time, in-situ monitoring of PEMWE cell and stack health is needed to detect and predict degradation pathways and bubble-related transport limitations without interrupting operation. Improved diagnostics tools, either hardware or software, can feed prognostic information into adaptive or model-predictive controllers, enabling dynamic adjustment of operating conditions. This is particularly critical to develop adapted tools with satisfactory performance under intermittent and dynamically varying renewable power supply. The diagnostic tools reflecting spatial heterogeneity of large stacks are also highly required given that the power scale of industrial electrolyzer installations shows a clear upward trend.

- Bubble management and thermal management are two key elements in PEMWE system control design. Since the accumulation and transport of oxygen bubbles within channels and PTL strongly affect local mass transport, ohmic resistance, and overall cell efficiency, Future research should focus on improving bubble removal through both passive strategies (e.g., tailored flow-field geometries, surface modifications, and hydrophilic/hydrophobic patterning) and active methods (e.g., controlled water flow and temperature, pressure regulation, pulsed operation, vibration-assisted detachment, and magnetic fields). Systematic studies that integrate in-operando diagnostics and multiphysics modeling will be essential to establish reliable bubble management strategies that enhance both efficiency and durability. Heat generation in PEM electrolysis, particularly at high current densities, can significantly influence cell performance and durability. Future designs must incorporate advanced cooling strategies, suitable thermal interface materials, and optimized flow-field architectures to ensure uniform temperature distribution and minimize local overheating and thermal gradients. Coupling electrochemical models with thermo-fluid simulations will be crucial to guide these developments and to enable predictive design and control of next-generation systems.

  At the system level, Research should therefore address the integration of short-term energy storage, such as batteries or supercapacitors, to buffer intermittent inputs and provide stable operation of PEM electrolysis. Such hybrid configurations can reduce transient stresses, improve dynamic efficiency, and extend component lifetime. Research efforts must also focus on integration, scalability, and techno-economic considerations. Seamless integration with renewable energy sources requires not only power-electronic interfaces but also intelligent energy management frameworks that account for degradation status and cost. Scaling up from laboratory cells to industrial stacks introduces challenges of uniform reactant distribution, effective bubble and thermal management, and reliable balance-of-plant components and their corresponding controls. Future studies should also embed techno-economic optimization into research pipelines, ensuring that advances in efficiency, durability, or bubble/thermal management directly translate into lower hydrogen production costs.

In summary, the prospects for PEM water electrolysis lie in a concerted, multidisciplinary effort to bridge remaining gaps at both the micro and macro scale. By uniting deeper materials insight, high-fidelity modeling, real-time diagnostics, bubble and thermal management, adaptive control, hybridization with batteries for stable renewable integration, and techno-economic evaluation, researchers can significantly accelerate progress toward more efficient, durable, and scalable PEM electrolysis systems. These developments will not only advance the scientific state-of-the-art but also pave the way for the widespread deployment of PEM electrolysis in the emerging clean hydrogen economy.

8. Conclusion

This review provides an integrated perspective on PEM electrolysis, emphasizing optimal operation as the guiding objective across both cell and system levels. Achieving such operation requires balancing efficiency with durability, reliability. To address these intertwined challenges, we introduce an Integrated Optimization Framework that unifies insights from materials, degradation, modeling, diagnostics, and control into a coherent roadmap. This framework places optimal operation at the forefront of both current understanding and future development.

Materials and components form the foundation for optimal performance. Careful design of membranes, catalysts, bipolar plates, and porous transport layers is essential for minimizing losses and withstanding harsh conditions. For example, resilient membranes and optimized catalyst loadings reduce degradation under high currents and temperatures, thereby extending lifetime while preserving efficiency. Degradation mechanisms provide critical guidance for sustaining optimal conditions. Identifying and quantifying chemical, mechanical, and thermal failure modes enables targeted mitigation through improved materials and controlled operating regimes. In practice, this knowledge allows the PEMWE to be run continuously within its most reliable and efficient window. Modeling supplies the predictive insights necessary for optimization. From simple lumped models to multi-dimensional, physics-based approaches, these tools simulate system behavior across operating conditions. By incorporating degradation kinetics, models make it possible to forecast long-term performance and to identify operational setpoints that maximize efficiency while preventing premature aging. Diagnostics ensure the system remains within its optimal operating regime. Combining electrochemical and physical techniques provides a comprehensive view of performance losses and structural changes. Continuous monitoring and early fault detection enable adaptive responses, so that efficiency and durability are preserved in real time. Control closes the loop by actively steering the system toward optimal operation. Advanced strategies dynamically regulate current, temperature, flow, and pressure, ensuring safe, efficient, and degradation-aware operation even under fluctuating renewable inputs. In doing so, control integrates all other modules-materials, degradation knowledge, modeling, and diagnostics-into a unified operational strategy.

Taken together, these elements converge in the proposed Integrated Optimization Framework, which explicitly links component design, degradation science, predictive modeling, system diagnostics, and control into a holistic strategy. This framework provides both an academic foundation and a practical pathway for enhancing the efficiency, durability, and reliability of PEM electrolysis. By explicitly centering optimal operation as the unifying objective, the review addresses existing gaps in the literature and outlines a roadmap for advancing PEM technology toward its full potential as a cornerstone of the hydrogen economy.

Table 6: Nomenclature for PEM Electrolysis Modeling Methods

Abbreviation / Symbol	**Definition**
PEM	Proton Exchange Membrane
PEMWE	Proton Exchange Membrane Water Electrolysis
AEM	Anion Exchange Membrane Electrolysis
AWE	Alkaline Water Electrolysis
SOE	Solid Oxide Electrolysis
BoP	Balance of Plant
BPs	Bipolar Plates
DC bus	Direct Current bus
DC/DC	Direct Current to Direct Current (converter)
GDLs (or PTLs)	Gas Diffusion Layers (Porous Transport Layers)
HER	Hydrogen Evolution Reaction
OER	Oxygen Evolution Reaction
MEA	Membrane Electrode Assembly
PFSA	Perfluorosulfonic Acid

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AST	Accelerated Stress Test
EPMA	Electron Probe Microanalysis
FRR	Fluoride Release Rate
OCV	Open Circuit Voltage
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
EIS	Electrochemical Impedance Spectroscopy
CV	Cyclic Voltammetry
XRD	X-ray Diffraction
CFD	Computational Fluid Dynamics
PID	Proportional, Integral, and Derivative
MPC	Model Predictive Control
SMC	Sliding Mode Control

ΔG	Gibbs free energy
ΔH	Thermal energy requirement (enthalpy)
ΔS	Entropy charge
T	Temperature (K)
V_{cell}	Electrolysis cell voltage (V)
n	Number of electrons transferred during the reaction
F	Faraday constant (96485 C/mol)
V_{rev}	Reversible voltage (V)
V_{cons}	Mass transport overpotential (V)
V_{act}	Activation overpotential voltage (V)
V_{ohm}	Ohmic voltage (V)
V_{bub}	Voltage caused by bubble effect (V)
V_0	Standard reversible potential (V)
R	Gas constant (8.314 J/mol K)
P_{H_2}	Partial pressure of hydrogen
P_{O_2}	Partial pressure of oxygen
P_{H_2O}	Partial pressure of water
α	Charge transfer coefficient
i	Current (A)
i_0	Exchange current density
$i_{\text{0,ref}}$	Exchange current density at reference temperature
E_{act}	Activation energy of the electrode
I_{lim}	Maximum current that the electrolysis can receive
$V_{\text{act,cov}}$	Activation overpotential due to bubble coverage
$V_{\text{co,cov}}$	Concentration overpotential due to bubble coverage
$V_{\text{ohm,cov}}$	Ohmic overpotential due to bubble coverage
Θ	Bubble coverage area
A	Active sites area
r, s, t, d_1, d_2, r_1, r_2, s_1, s_2, t_1, t_2, t_3	Empirical parameters (dimensionless)
δ	Thickness of the membrane material
σ_m	Membrane conductivity
λ_m	Degree of membrane humidification (dimensionless)
C	Concentration

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