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Review article

Dynamic operation of proton exchange membrane electrolyzers—Critical review

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ABSTRACT

Green hydrogen is seen as a promising energy storage and balancing solution to complement the ever-increasing share of variable renewable energy sources in the grid. The dynamic operation of polymer electrolyte membrane (PEM) electrolyzers has the potential to simultaneously lower the cost of green hydrogen and improve the flexibility of the grid by taking advantage of the volatility of renewable production. However, dynamic operation affects a wide range of variables related to the degradation of electrolyzer components and the safety and efficiency of the process, often in counterintuitive ways. This, in turn, makes it difficult to predict the levelized cost of the green hydrogen produced when operating on the electricity markets. This critical review examines state-of-the-art literature on the behavior of PEM electrolyzers under dynamic operation, bearing in mind the objective of reducing the levelized cost of green hydrogen. Knowledge gaps, key development directions, and future research needs are identified with respect to PEM electrolysis equipment, operating parameters, degradation, and the role of dynamically operated PEM electrolyzers on the electricity markets. It is found that while the field is developing at a rapid pace, there is a lack of holistic studies that consider all (or even most of) the interconnected variables that affect the levelized cost of green hydrogen during the dynamic operation of PEM electrolyzers. It is postulated that this complex network of interactions will give rise to data-driven approaches (such as Machine Learning) to bridge this gap.

1. Introduction

One of the major contributors to global warming is the energy sector which is responsible for roughly three quarters of global greenhouse gas emissions [1,2]. Although electrification plays a significant role in decarbonizing this sector, its implementation still faces many challenges. The intermittent nature of variable renewable energies (VRE) affects the stability and reliability of the electric grid [3–5]. In addition, some aspects of the energy sector are hard to electrify: aviation, maritime shipping, heavy transport vehicles, and the heavy industry [6–8].

Green hydrogen, produced through electrolysis using emission-free energy sources, can contribute to solving these challenges by replacing fossil-based hydrogen in chemical processes or as a feedstock for producing different near carbon neutral e-fuels via power-to-X technologies. These e-fuels can be used directly to decarbonize hard-to-electrify sections of the energy sector [9–11].

For limiting the temperature rise to 1.5 °C, the International Renewable Energy Agency (IRENA) estimates that the share of VRE production in the electricity grid needs to increase from 7% in 2018 to 42% in 2030 and 63% in 2050. Further, IRENA projects that the capacity of water electrolyzers needs to increase from 458 MW in 2021 to 350 GW in 2030 [12]. This increase in electrolysis capacity could either add more stress to the electricity grid or be exploited as an opportunity through the dynamic operation of electrolyzers. The dynamic operation of electrolyzers can improve stability and flexibility of the electric grid by providing more demand response capabilities [9,13,14]. Moreover, producing green hydrogen when VRE is abundant and electricity prices are low has the potential to reduce the levelized cost of green hydrogen [15,16]. However, frequent fluctuations with short intervals during the dynamic operation of electrolyzers accelerate their degradation [17–19]. Therefore, it is important to understand and optimize the dynamic operation of electrolyzers for them to add value to a decarbonized energy system.

This paper focuses exclusively on the dynamic operation of polymer electrolyte membrane (PEM) electrolyzers. Although alternative options for direct water splitting exist which require less electrical energy per unit of green hydrogen produced and operate at a lower voltage than direct water electrolysis (such as SO_2-depolarized electrolysis), their technology readiness level is still low and they are excluded from this review [20–22]. PEM electrolysis was chosen as the sole subject of this review due to its superior dynamic characteristics compared to

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Nomenclature

Abbreviations

AEL	Alkaline electrolyzer
HER	Hydrogen evolution reaction
IRENA	International Renewable Energy Agency
MEA	Membrane electrode assembly
OER	Oxygen evolution reaction
PEM	Polymer electrolyte membrane
PTL	Porous transport layer
RF	Ripple factor
SOEL	Solid oxide electrolyzer
VRE	Variable renewable energy

Symbols

a_{H_2O}	Activity of water fed in liquid state, –
α	Charge transfer coefficient, –
C	Electric capacitance value, farad
ΔG	Gibbs free energy, J
η_{elec}	Electrical efficiency, –
E_{OC}	Open circuit voltage, V
E_{rev}	Reversible voltage, V
F	Faraday constant, C mol^{-1}
η_f	Faraday efficiency, –
i	Current density, A m^{-2}
i_0	Exchange current density, A m^{-2}
I_{AC}	Alternating (ripple) current component, A
I_{DC}	Direct current component, A
I_{el}	Effective electrolyzer current, A
I_{in}	Input current, A
i_L	Limiting current density, A m^{-2}
I_{RMS}	Root mean square current, A
n	Number of electrolyzer cells in series, –
p	Operating pressure, Pa
P_{H_2}	Electric power converted to hydrogen, W
p_{H_2}	Partial pressure of hydrogen, Pa
P_{in}	Input electric power, W
p_{O_2}	Partial pressure of oxygen, Pa
R	Universal gas constant, J K^{-1} mol^{-1}
R_X	Electric resistance of component X, Ω
T	Operating temperature, K
t	Operating time, s
τ	Time constant, s
U_{th}	Thermoneutral voltage, V
U_{act}	Activation overvoltage, V
U_{diff}	Diffusion overvoltage, V
U_{in}	Input voltage, V
U_{ohm}	Ohmic overvoltage, V
V_{actual}	Actual volume of hydrogen produced, m^3
η_v	Voltage efficiency, –
$V_{theoretical}$	Theoretical volume of hydrogen produced, m^3
X_a	Subscript a indicates anode side, –
X_c	Subscript c indicates cathode side, –
z	Number of electrons involved in the reaction, –

Table 1
Load flexibility and start-up times of different water electrolysis technologies.

	AEL	PEM	SOEL	Reference
Load flexibility (% of nominal load)	20%–100%	0%–100%	−100%–+100%	[23,24]
Warm start-up	1–5 min	<10 s	15 min	[23]
Cold start-up	1–2 h	5–10 min	hours	[23]

other direct water splitting technologies. As can be seen in Table 1, PEM electrolysis has lower response times than alkaline electrolysis (AEL) and solid oxide electrolysis (SOEL), which enables PEM electrolysis to react faster to the fluctuations in electricity production than AEL and SOEL, making it a better candidate for dynamic operation with VRE.

In recent years, research interest in water electrolysis has been increasing exponentially. However, the percentage of publications regarding PEM electrolysis only covers 15% of the total publications about water electrolysis and only 11% of these publications are related to the dynamic operation of PEM electrolysis [25]. In addition, according to the authors' knowledge, there is no literature review that focuses on the dynamic operation of PEM electrolyzers. The novelty of this critical review is exploring the state-of-the-art literature on the dynamic operation of PEM electrolyzers and identifying areas that need further research from multidisciplinary perspectives, bearing in mind the overarching objective of minimizing the levelized cost of green hydrogen. First, the fundamentals of PEM electrolysis and state-of-the-art electrolyzers and their materials are reviewed in Section 2. Next, state-of-the-art literature related to different interconnected variables affecting the dynamic operation of PEM electrolysis in terms of operating characteristics, degradation, and electricity markets is reviewed and discussed in Sections 3–5. These sections also present the research gaps and opportunities identified by the authors. Finally, conclusions are presented in Section 6. Based on the identified shortcomings of the literature, this review found that holistic approach to optimize the levelized cost of green hydrogen produced by the dynamic operation of PEM electrolyzers is needed to ensure the reduction of green hydrogen levelized cost. In such an approach, all interconnected variables should be considered together, preferably using data-driven methodologies.

2. PEM electrolysis

PEM electrolyzers operate according to the same principles as other water electrolysis technologies: water is electrochemically split into hydrogen and oxygen in the presence of electrical energy. A PEM electrolyzer consists of three main parts, as shown in Fig. 1: anode, cathode, and proton conducting membrane [26,27]. Water is fed into the anode where it splits into protons, electrons, and oxygen. This reaction is called the oxygen evolution reaction (OER) [28].

$$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^- \quad (1)$$

Next, protons move to the cathode through the proton conducting membrane, and electrons transfer to the cathode through a power source. At the cathode, electrons and protons combine to produce hydrogen. This reaction is called the hydrogen evolution reaction (HER) [28].

$$2H^+ + 2e^- \rightarrow H_2 \quad (2)$$

The global reaction of a PEM electrolyzer is as follows [28]

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \quad (3)$$

Green hydrogen produced via water electrolysis has a high purity, with the only side product being oxygen [28]. In addition, harmful emissions associated with green hydrogen production are limited to

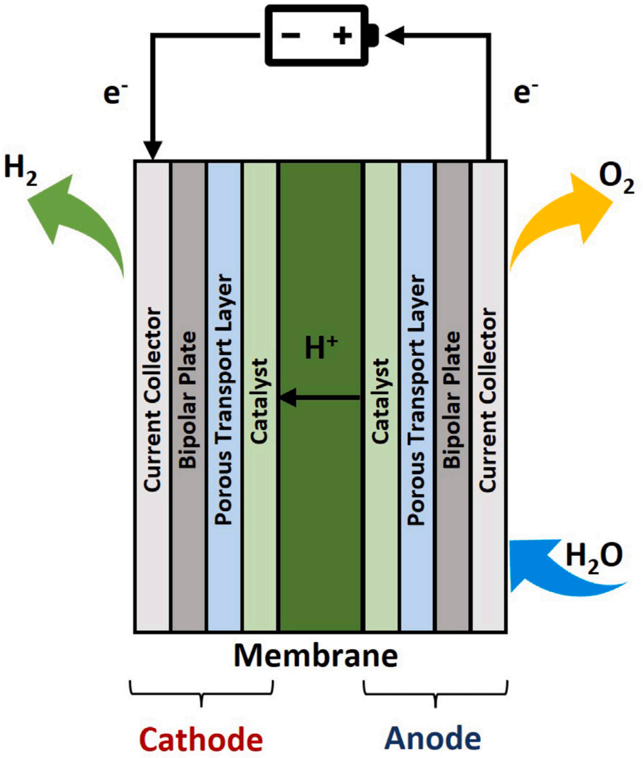

Fig. 1. Main components of a proton exchange membrane (PEM) electrolyzer cell.

those arising from the production of the renewable electricity source and manufacturing of the electrolyzer [29,30].

PEM electrolyzer development efforts focus on decreasing the cost and increasing the reliability and efficiency of materials used in the anode, the cathode, and the proton exchange membrane [27,31]. A PEM electrolyzer stack consists of current collectors at both ends, bipolar plates, and membrane electrode assembly (MEA) where the active material electrodes are painted on top of the polymer electrolyte membrane [32,33]. Fig. 1 shows the components of a single cell of a PEM electrolyzer stack. The cell consists of current collectors, bipolar plates, porous transport layers (PTL), catalyst layers, and polymer electrolyte membrane.

2.1. Anode

Anode material development is very challenging, as the anode environment is highly oxidative. Moreover, the OER is slower than the HER, and it requires a higher activation energy [34,35]. Therefore, a higher electric overpotential is applied to the anode electrodes. Thus, materials used in anode electrocatalysts should be highly active, corrosion resistant, and should be able to withstand high electric potential to improve the relabilty and efficiency of the electrolyzer. These conditions place limitations on the range of materials that can be used [34]. Currently, noble rare metals, especially iridium-based and ruthenium-based catalysts, are seen as the most suitable materials. Although ruthenium-based catalysts are more active and less expensive than iridium-based catalysts, they have a higher corrosion rate. Therefore, iridium is the most used material in manufacturing anode electrocatalysts [34,36]. While the anode catalyst accounts for only 6% of the PEM electrolyzer stack cost, future supply of iridium could be a bottleneck in the large-scale deployment of PEM electrolysis [31,37].

Iridium accounts for less than 3% of the Platinum group metals mined in South Africa and Zimbabwe where about 95% of iridium production takes place. In 2022, the global annual demand of iridium was only 7.9 tonnes [38]. Kiemel et al. [39] modeled the capacity of electrolyzers needed in Germany for reducing GHG emissions by 85% until 2050 along with the required critical materials for achieving this target. When assuming a constant iridium loading (0.667 g/kW), 80% recycling efficiency after the end of life of the electrolyzers, and a 40% market share of PEM electrolyzers in 2050, it was found that about 37% of the global iridium production in 2016 (2650 kg) will be needed for satisfying the needs of the added capacity in Germany by 2050. However, if a technological advancement in iridium loading is considered (projected to be as low as 0.05 g/kW in 2035), the iridium demand in 2050 will decrease to about 200 kg and peak in 2027 at about 500 kg (about 3% and 7% of 2016 production, respectively).

Moreover, when Kiemel et al. increased the scope of their analysis to include critical materials required globally for electrolyzers, it was found that, in the scenario where technological advancement can be achieved, about 45% of 2016 iridium production will be needed to satisfy the global demand in 2050 with a peak in 2027 around 113%. The cumulative global electrolysis capacity in this scenario is 3400 GW, which is the lower end value in the study. The upper end estimate of 9900 GW seems to be rather high, as the upper end estimate in another study by the Hydrogen Council and McKinsey & Company for a net-zero emissions economy scenario is 4000 GW electrolysis capacity in 2050 [40], more in alignment with the lower end estimate of the Kiemel et al. study [39]. Kiemel et al. estimated that lifespan of PEM electrolyzers will increase from 20 to 27 years by 2050. Although a shorter lifespan can decrease the severity of iridium supply shortage by allowing more iridium to be recycled, it also decreases the electrolyzer capacity factor. This, in turn, can increase the levelized cost of green hydrogen if operation is not correctly optimized. Moreover, the possibility of recycling iridium from other industries was not included in the study.

Therefore, current research focuses mainly on reducing the loading of iridium in anode electrocatalysts. Inert elements (such as molybdenum, tantalum, and tin) and active elements (such as ruthenium) are doped into the iridium oxide solid solution. Using inert elements improves the stability and decreases the activity of the catalyst [41,42]. Therefore, a compromise between cost, activity, and stability must be reached. Moreover, developing iridium free catalysts have been studied extensively, particularly unary metal oxides (such as manganese oxides, cobalt oxides, and iron oxides). Thus far, none of the unary metal oxides achieved stability and activity comparable to iridium based catalysts [42]. Therefore, focus has recently shifted to polymetallic mixtures where various compositions of non-precious metals are designed to enhance the activity and stability of the catalyst. Patel et al. [43] succeeded in developing a fluorine doped copper manganese oxide catalyst which has a comparable activity to iridium based catalysts along with a good long term stability. Despite the promising results that started to emerge from this area, more research is needed to confirm the reported outputs and to establish the long term stability of catalysts under both constant and dynamic operation.

Other components of the anode, the current collector, the bipolar plate, and the PTL should be corrosion resistant and have high electrical conductivity [27,28]. The geometry of components plays an important role in the efficiency of a PEM electrolyzer, because at higher current densities, mass transfer becomes a limiting factor. Increasing porosity improves mass transfer within the anode, but it simultaneously decreases the electrical conductivity [28,44]. Therefore, more research is needed for optimizing the geometry of the components and their resulting flow fields.

Overall, current anode material development primarily focuses on reducing the capital cost of the anode and decreasing the demand of iridium in PEM electrolyzers. To do so, research focuses on using cheaper support materials with coating for protection from the harsh environment, reducing the loading of noble metals in the electrocatalysts, and utilizing nanostructured materials and mixed metal oxides [31,45].

2.2. Cathode

Although the environment is less harsh at the cathode than at the anode, cathode material development is still needed to improve the efficiency and reduce the cost of PEM electrolyzers. The cathode environment is not oxidative, and the HER requires less electric overpotential than the OER. This enables the utilization of less expensive, non-noble metals in cathode electrocatalysts, such as transition metal compounds and carbonaceous materials [46,47]. However, noble-metal-free electrocatalysts, or those with ultra low loading of noble metals (such as less than 0.02 mg cm^{-2} Pt-loading [48]) still suffer from significantly lower activities and stabilities than commercially used noble-metals-based electrocatalysts. This increases operational cost, electricity use, and maintenance cost, which outweighs the cost savings from reducing noble metal content [41]. However, more research emphasis should be placed on improving the activity and stability of cathode electrocatalysts that have an ultra low loading (or a complete lack) of noble metals. With the expected increase in the global demand for PEM electrolyzers in the coming years, the supply of noble metals used in cathode electrocatalysts (such as platinum) can act as a bottleneck for scaling up the production of PEM electrolyzers [39]. Currently, platinum- and palladium-based nanoparticle electrocatalysts on less expensive support materials, such as platinum supported on carbon (Pt/C), are used commercially [28,41].

Although the cathode catalyst currently accounts for only 2% of the PEM electrolyzer stack cost, platinum demand can also affect the large-scale deployment of PEM electrolysis [31,39]. Kiemel et al. [39] assigned a high risk rating to the supply of platinum, because the current demand already exceeds the supply from primary production. In addition, PEM electrolyzers will be competing with other industries where platinum is widely used. However, this issue can be tackled by increasing the recycling of platinum through improving the economic viability of the recycling process and introducing legislation that encourages platinum recycling. In the last 6 years, only 25% of platinum demand was supplied by recycling, although platinum recycling efficiency can reach as high as 95% [38,49].

While reducing the cost and increasing the efficiency of electrocatalysts is instrumental in achieving economic viability for green hydrogen, it is worth mentioning that titanium has the highest cost contribution of any material in PEM electrolyzers, accounting for about 50% of the stack cost [16]. This is mainly due to its high manufacturing cost. Titanium is used in bipolar plates and PTLs. Therefore, reducing the manufacturing and material cost of these components is also an essential piece of the puzzle.

2.3. Membrane

The proton exchange membrane is a critical part of a PEM electrolyzer. It allows the transport of protons from the anode to the cathode and prevents the transport of gaseous molecules — oxygen from the anode to the cathode and hydrogen from the cathode to the anode [27,28]. Currently, the most commercially used materials for proton exchange membranes are Perfluorosulfonic acid polymers such as Nafion™. Nafion™ has high strength, high stability, high proton conductivity, low gas permeability, and it withstands high current densities [27,28]. However, it also has a high cost, as it accounts for about 5% of PEM electrolyzer stack cost. Besides, the manufacturing cost of the MEA accounts for 10% of the stack cost [31]. Material development for proton exchange membranes focuses on using cheaper materials and reducing the thickness of the membrane without compromising stability, safety requirements, and proton conductivity.

When gaseous molecules pass through the membrane, oxygen molecules recombine with hydrogen to produce water and hydrogen peroxide. This decreases the efficiency of the electrolyzer and accelerates its degradation [50,51]. Moreover, a gaseous mixture of hydrogen and oxygen is combustible, presenting a safety hazard when the volumetric percentage of hydrogen in oxygen reaches 4%. Therefore, a PEM electrolyzer shuts down when the volumetric percentage of hydrogen at the anode reaches 2% [50,52]. The trade-offs mandated by these process safety considerations warrant further discussion: hydrogen, when used in chemical processes or as a feedstock for producing e-fuels, must often be supplied at high pressure [53–55]. Ayers et al. stated that electrochemical compression of hydrogen via accumulating hydrogen gas on the cathode side of a PEM electrolyzer (up to 700 bar) is more efficient than mechanical compression [56]. However, increasing the pressure difference between the cathode and the anode increases the penetration of hydrogen molecules to the anode [57], leading to the increase of the safety risks. Therefore, for improved electrolysis efficiency and safe operation, proton exchange membranes should be designed to prevent hydrogen penetration even at elevated pressure differences if hydrogen needs to be supplied at high pressures.

Bukola and Creager [58] reported that embedding a single layer of graphene in the middle of a Nafion™ membrane decreases the penetration of hydrogen molecules to the anode up to eight-fold while slightly decreasing the proton conductivity. This can enable reducing the thickness of the membrane beyond the current state-of-the-art even at elevated pressure differences between the cathode and the anode. Decreasing the membrane thickness without compromising safety standards simultaneously decreases the cost and improves the proton conductivity of the membrane. In addition, Ion-Ebrasu et al. [59] reported that doping graphene into a Fumapem™ membrane improves water intake in the membrane, which in turn improves the proton conductivity. However, long-term stability and the crossover of gaseous molecules should be studied further. Graphene is a promising material for further research in order to reduce the cost, improve the proton conductivity, and decrease the crossover of gaseous molecules through the membrane. These properties can enhance the ability of the PEM electrolyzer to follow the production of VRE, even at low production times and high cathode–anode pressure differences.

3. Dynamic operation characteristics

This section begins with a brief overview of the interaction between the key operating parameters: current, voltage, temperature, and pressure, to provide a basis for discussing the effect of dynamic operation on PEM electrolyzers. In an electrical equivalent model, complex systems can be simplified by approximating different physical properties and losses using electrical components [60,61]. PEM electrolyzers can be modeled using different combinations of resistance, capacitance, and voltage source.

Since a PEM electrolyzer is operated using direct current [62], the input power needed is the product of input current and voltage [63].

$$P_{in} = I_{in} \cdot U_{in} \tag{4}$$

The relation between input current from the power source (I_{in}) and useful current in the electrolyzer (I_{el}) is determined by the Faraday efficiency (η_f) [64]

$$\eta_f = \frac{I_{el}}{I_{in}} \tag{5}$$

where η_f represents losses due to short-circuit currents and the transport of gases through the membrane. Because the value of η_f is usually close to 1, it is often neglected when modeling electrolyzer behavior [64,65]. However, at low current densities, η_f value decreases significantly. In addition, η_f changes with electrolyzer temperature and pressure [66,67]. η_f can be experimentally calculated by dividing the measured volume of hydrogen produced by the theoretical volume of hydrogen when the input current is assumed to be equal to the electrolyzer current [27,66].

$$\eta_f = \frac{V_{actual}}{V_{theoretical}} \tag{6}$$

where

$$V_{theoretical} = \frac{R \cdot T \cdot I_{in} \cdot t}{F \cdot p \cdot z} \tag{7}$$

R is the universal gas constant, T is the electrolyzer operating temperature, t is the electrolyzer operating time, F is the Faraday constant, p is the electrolyzer operating pressure, and z is number of electron moles involved in the reaction.

For the electrolysis reaction to occur, the applied voltage needs to overcome open-circuit voltage and various overvoltages [64,68].

$$U_{in} = n(E_{OC} + \Delta U_{act} + \Delta U_{\mathrm{ohm}} + \Delta U_{diff}) \tag{8}$$

n is the number of cells in series, E_{OC} is the open-circuit voltage, U_{act} is the activation overvoltage, U_{ohm} is the ohmic overvoltage, and U_{diff} is the diffusion overvoltage.

The open-circuit voltage can be calculated by the Nernst equation by taking into account the operating temperature, the activity of the reactant and the partial pressure of products [64,68]. Assuming that products are ideal gases, these equations take the following form:

$$E_{OC} = E_{rev} + \frac{R \cdot T}{z \cdot F} ln(\frac{p_{\mathrm{H_2}} \cdot p_{\mathrm{O_2}}^{\frac{1}{2}}}{a_{\mathrm{H_2O}}}) \tag{9}$$

and

$$E_{rev} = \frac{\Delta G_{T,p_{ref}}}{z \cdot F} \tag{10}$$

where E_{rev} is reversible voltage, $p_{\mathrm{H_2}}$ is the partial pressure of hydrogen, $p_{\mathrm{O_2}}$ is the partial pressure of oxygen, $a_{\mathrm{H_2O}}$ is the activity of water fed in the liquid state, and ΔG is the Gibbs free energy at the electrolyzer operating temperature and reference pressure.

U_{act} represents electromagnetic field losses caused by the transfer of electrons between the electrolyte and the electrodes on both the anode and the cathode sides. U_{act} can be modeled using the Tafel equation [64,66]:

$$\Delta U_{act,a} = \frac{R \cdot T}{\alpha_a \cdot z \cdot F} ln(\frac{i_a}{i_{0,a}}) \tag{11}$$

$$\Delta U_{act,c} = \frac{R \cdot T}{\alpha_c \cdot z \cdot F} ln(\frac{i_c}{i_{0,c}}) \tag{12}$$

$$\Delta U_{act} = \Delta U_{act,a} + \Delta U_{act,c} \tag{13}$$

where $U_{act,a}$ and $U_{act,c}$ represent the activation overvoltage, α_a and α_c are the charge transfer coefficients, i_a and i_c are the current densities, and $i_{0,a}$ and $i_{0,c}$ are the exchange current densities. Subscripts a and c represent the anode and the cathode, respectively.

U_{ohm} represents losses due the movement of electrons through the PEM electrolyzer (electrical losses) and the movement of protons through the membrane (ionic losses). Electrical losses occur in both electrodes, the PTL, the bipolar plates, and in the current collector [66,69]. U_{ohm} is calculated using Ohm's law [64]:

$$\begin{aligned}\Delta U_{\mathrm{ohm}} = I_{el}(&R_{membrane} + R_{electrodes} + R_{PTL} + R_{bipolarplates} \\ &+ R_{currentcollectors})\end{aligned} \tag{14}$$

where U_{diff} represents mass transport limitations. When the concentration of products (H_2 and O_2) increases, the reaction rate decreases [64,66]. The anode U_{diff} is much higher than the cathode U_{diff}, since the anode reaction rate is slower than the cathode reaction rate and requires more energy [34,46]. U_{diff} can be modeled using the Limiting Current technique [64,70]:

$$\Delta U_{diff,a} = \frac{R \cdot T}{\alpha_a \cdot z \cdot F} ln(\frac{i_L}{i_L - i_a}) \tag{15}$$

$$\Delta U_{diff,c} = \frac{R \cdot T}{\alpha_c \cdot z \cdot F} ln(\frac{i_L}{i_L - i_c}) \tag{16}$$

$$\Delta U_{diff} = U_{diff,a} + U_{diff,c} \tag{17}$$

where $U_{diff,a}$ and $U_{diff,c}$ are the diffusion overvoltages of the anode and the cathode respectively, and i_L is the limiting current density.

During dynamic operation, in transient state, the electrical frequency is no longer zero. Therefore, the capacitive nature of the anode and cathode electrodes affects the voltage change in transients [71,72]. Although PEM electrolyzers have a fast response to changes in input electricity, over/under-voltage of the activation voltage occurs in the transient state until steady state is reached again [73,74]. This over/under-voltage occurs due to the dynamics of the reaction at the anode and the cathode. This, in turn limits the change of activation voltage during a transient as follows [66]:

$$\frac{dU_{act,a}}{dt} = \frac{I_{el}}{C_a} - \frac{1}{\tau_a} \cdot U_{act,a} \tag{18}$$

and

$$\frac{dU_{act,c}}{dt} = \frac{I_{el}}{C_c} - \frac{1}{\tau_c} \cdot U_{act,c} \tag{19}$$

where C_a and C_c are the anode and cathode capacitance values respectively, and τ is the time constant which is equal to the product of the resistance and the capacitance of the electrode [66,71]. According to Guilbert et al. [73], during a transient state, the discrepancy between experimental data and the steady state model can be as high as 15%. However, when the dynamic nature of electrolyzer is considered in the model, the maximum discrepancy drops to 4%. Transients can occur when VRE production changes or due to quality issues of power electronics [71,75]. Dynamic models are still very limited, especially when considering different devices used in the electrolysis process other than the electrolyzer, such as pumps, compressors, heat exchangers, power converters, and separators. Therefore, more research is needed in dynamic modeling of PEM electrolysis, to have full understanding of the effect of transient state on PEM electrolysis operation.

The power converted to hydrogen can be calculated using a relation between electrolyzer current and open circuit voltage [64,68,71]. As can be seen, in equations from (8) to (17), increasing the electrolyzer current increases the required electrolyzer voltage because overvoltage losses increase, while E_{OC} remains constant. However increasing electrolyzer current increases hydrogen production, as shown in Eq. (20).

$$P_{\mathrm{H_2}} = n \cdot I_{el} \cdot E_{OC} \tag{20}$$

3.1. Efficiency

In this section, the effect of dynamic operation on the efficiency of PEM electrolyzers will be discussed. Three main variables are used for describing the efficiency of a PEM electrolyzer: electrical efficiency (η_{elec}), voltage efficiency (η_v), and Faraday efficiency (η_f), as described earlier. η_{elec} is the ratio of the power of the produced hydrogen to the input electric power. η_v is the ratio between thermoneutral voltage and input voltage [66,71].

$$\eta_{elec} = \frac{P_{\mathrm{H_2}}}{P_{in}} \tag{21}$$

$$\eta_v = \frac{U_{th}}{U_{in}} \tag{22}$$

where

$$\eta_{elec} = \eta_f \cdot \eta_v \tag{23}$$

Increasing the input current decreases η_v and increases η_f [76,77]. However, the effect of input current on electrical efficiency also depends on initial current density and pressure. At a very low current density and a high differential pressure, the increase in η_f is greater than the decrease in η_v, which improves the electrical efficiency. Conversely, at a higher current density and a high differential pressure, the decrease in η_v is higher, which reduces the efficiency [67]. However, at ambient pressure, the decrease in η_v dominates, and efficiency is inversely proportional to the input current [78]. Fig. 2 shows how

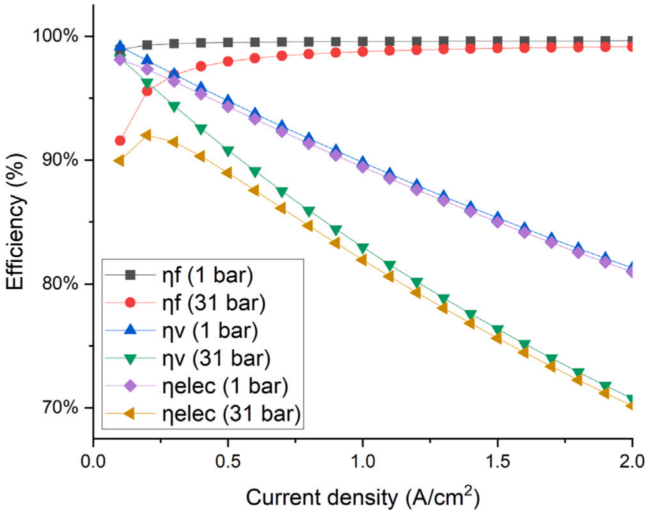

Fig. 2. Relation between proton exchange membrane electrolyzer efficiency and current density at various pressures and a temperature of 60 °C. η_f is Faraday efficiency, η_v is voltage efficiency, and η_{elec} is electrical efficiency.
Source: Data calculated from [79,80].

the electric-, voltage-, and Faraday efficiencies change with current density at different pressures. Faraday efficiency was calculated using experimental data from Trinke et al. [79], while PEM electrolyzer voltage was calculated using empirical equations developed by Atlam and Kolhe [80]. In these calculations, only the PEM electrolyzer cell efficiency is considered at $T = 60$ °C.

η_v decreases because increasing current density increases the detachment diameter of gas bubbles, which, in turn, decreases the catalyst area exposed to the electrolysis reaction and increases ΔU_{act} overvoltage losses [81]. Moreover, gas bubbles also affect the passivation of metals in the PTL and the bipolar plates. Frequent formation and detachment of gas bubbles near the PTL and the bipolar plates causes the detachment of anti-corrosion coating materials, leading to the passivation of the PTL and the bipolar plates. As current density increases, the detachment of anti-corrosion materials accelerates, increasing ΔU_{ohm} overvoltage losses [82–84]. Therefore, more anti-corrosion coating for the PTL and the bipolar plates is needed for operating PEM electrolyzers at higher current densities. However, increasing the thickness of the anti-corrosion coating increases the capital cost of a PEM electrolyzer.

Another mechanism through which efficiency depends on pressure is the transport of hydrogen molecules from the cathode to the anode: increasing differential pressure facilitates this process and decreases the efficiency of the electrolyzer [67,85]. However, when the entire electrolysis process is accounted for, efficiency actually increases up to 700 bar, as discussed in Section 2.3. Next, while partial loading of a PEM electrolyzer improves the electrical efficiency, it decreases the capacity factor of the electrolyzer, leading to two counteracting effects on the levelized cost of the produced hydrogen.

In addition to partial loading, the dynamic operation of PEM electrolyzers is associated with changing input power over time. The frequency of fluctuations depends on the nature of the connected power source and the mode of operation. Fluctuations increase when the electrolyzer is directly connected to VRE sources without any storage or back-up power source. Lee at al. [86] found that the direction of fluctuation (i.e. whether the system is ramping up or down) and the rate of change affect gas bubble accumulation. The rate of gas bubble formation during ramping up is higher than bubble detachment rate during ramping down. Lingering gas bubbles can block water from reaching the membrane, leading to a decrease in the water content of the membrane. This, in turn, leads to a decrease in its ionic conductivity and an increase in ΔU_{ohm} overvoltage losses.

Conversely, gas bubbles near the catalyst layer decrease ΔU_{diff} overvoltage losses, since the formation of gas bubbles absorbs dissolved oxygen, decreasing its concentration and increasing the rate of the OER [87,88]. However, to achieve high efficiencies in PEM electrolysis with fluctating input power (especially during dynamic operation), the number of bubble nucleation sites should be maximized and the bubble detachment diameter should be minimized. This can be done by controlling the flow of input water, a sudden adjustment of operating pressure, or a sudden adjustment of input current or voltage [81,89]. Fig. 3 illustrates this concept: it shows the nucleation, growth, and detachment of gas bubbles in the catalyst layer along with the detachment of catalyst active sites from the catalyst layer due to the frequent formation and detachment of gas bubbles. When the detachment diameter of gas bubbles increases, stress at the interface between the catalyst and the gas bubbles increases, which accelerates the detachment of catalyst active sites and decreases the lifetime of the catalyst layer. When catalyst active sites are covered or detached, ΔU_{act} overvoltage losses increase. Therefore, more research regarding optimizing the flow fields arising in PEM electrolyzers during different modes of operation is recommended with the aim of maximizing the number of gas bubbles and minimizing their detachment diameter to ensure high efficiency and durability during dynamic operation.

Moreover, increasing load fluctuation within a given amount of time affects η_f. Any unidirectional current (I_{RMS}) consists of two components, a direct current component (I_{DC}) and an alternating (ripple) current component (I_{AC}) according to [90]:

$$I_{RMS} = \sqrt{I_{DC}^2 + I_{AC}^2} \tag{24}$$

In a pure direct current, I_{RMS} is equal to I_{DC} and I_{AC} is zero. Ripple factor (RF) is a ratio that measures the deviation of unidirectional current from pure direct current [91]:

$$RF = \frac{I_{AC}}{I_{DC}} \tag{25}$$

Buitendach et al. [90] investigated the effect of the ripple factor on power consumption and hydrogen production in a PEM electrolyzer. It was found that power consumption, which indicates the increase of input current, increases with increasing ripple factor. However, hydrogen production is solely dependent on I_{DC} and has no correlation with the ripple factor. The extra power consumed is dissipated in the form of heat, and does not drive the electrolysis reaction. Therefore, η_f decreases when RF increases. In addition, Buitendach et al. [90] suggested that the input waveform has no effect on efficiency and attributed the differences in efficiency between different waveforms at identical frequencies solely to the ripple factor. However, a comparison between different waveforms at the same ripple factor and frequency was not included in that study. This warrants further investigation, since different input current waveforms can affect gas bubble accumulation within the electrolyzer.

Finally, operating temperature also affects the efficiency of PEM electrolyzers. Increasing the temperature increases the ionic conductivity of the membrane along with reaction rates, which improves the overall efficiency [92]. However, it accelerates the degradation of the membrane, as will be discussed in Section 4.

3.2. Safety

This section discusses the effect of dynamic operation on the operational safety limits of PEM electrolyzers. The main safety issue related to operating a PEM electrolyzer is the crossover of hydrogen gas from the cathode to the anode. As mentioned in Section 2.3, when the volumetric percentage of hydrogen in oxygen reaches about 4%, the mixture becomes combustible. Therefore, the ratio is kept below 2% to assure safety [50,52,85]. Hydrogen penetration through the membrane is directly proportional to the electrolyzer current density. However, at low current densities, the amount of produced oxygen at

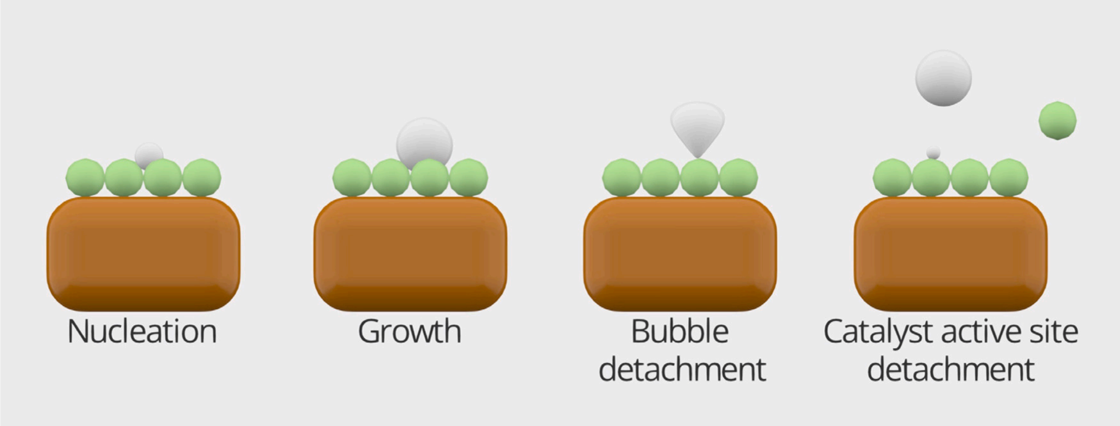

Fig. 3. Schematic of gas bubble nucleation, growth, and detachment with catalyst active site detachment. Gas bubble (White). Catalyst layer active sites (Green). Catalyst support (Brown).

the anode is low, which can lead to a higher hydrogen to oxygen ratio. At ambient pressure and a low operating temperature, the material and the thickness of the proton exchange membrane are designed to avoid this problem. However, Hydrogen penetration through the membrane increases with increasing operating temperature and differential pressure between the cathode and the anode, which sets a lower limit on the allowable input current [67,85,93].

Therefore, when a PEM electrolyzer is operated at an elevated temperature or pressure, the minimum operating load increases in comparison with ambient temperature and pressure. This impairs the ability of PEM electrolyzers to follow the production of VRE during periods of low production. In off-grid VRE systems without energy storage, electricity produced during these periods can thus be wasted instead of being utilized by the electrolyzer. Such waste of electricity increases the levelized cost of the electricity produced by the VRE plant, since capital and operating costs are the same while the amount of product sold decreases. The effect of differential pressure on the safety and the minimum operating load can be mitigated by pressurizing the hydrogen produced using a compressor outside the electrolyzer, and operating the electrolyzer without a pressure difference between the anode and the cathode. However, this decreases the overall electrolysis process efficiency, as discussed in Section 2.3. Moreover, it increases the capital and maintenance costs of the plant due to the increase in the number of components, which increases the levelized cost of the produced green hydrogen. Therefore, safety constraints should be considered when optimizing the dynamic operation of a PEM electrolyzer.

4. Degradation during dynamic operation

The degradation of a PEM electrolyzer refers to the gradual loss of its performance over its lifetime. It is useful to distinguish between reversible and irreversible degradation. The dynamic operation of a PEM electrolyzer can help prevent the accumulation of some reversible degradation. However, it also introduces more challenges that need to be understood and solved for efficient and safe operation [94,95]. Reversible degradation can be fixed by dynamic operation and by preforming regular preventive maintenance, for example the chemical removal of titanium passivation in the PTL and the bipolar plates [89,96]. Sudden change of input current or voltage helps by flushing oxygen bubbles from the anode, which improves the mass transport of water and protons and thus enhances the performance of the electrolyzer. In contrast, irreversible degradation, such as membrane thinning and iridium dissolution, is permanent. Therefore, irreversible degradation limits the lifetime of a PEM electrolyzer [89,97].

During dynamic operation, the operator needs to take decisions to follow the fluctuating power source, operate at a partial load or completely shut down the electrolyzer. This section discusses the potential effect of these decisions on degradation.

4.1. Load fluctuation

As discussed in Section 3.1, load fluctuation can increase the accumulation of gas bubbles and the ripple factor. When gas bubbles are formed near the catalyst layer, the frequent formation and detachment of gas bubbles induces stress on the catalyst-bubble interface. This stress can lead to the detachment of the active layer of the catalyst. Moreover, the accumulation of bubbles in the catalyst layer pores can affect its porous structure. Also, when gas bubbles are formed near the PTL or the bipolar plates, interfacial stress can detach anti-corrosion coating material, which speeds the corrosion of the PTL and the bipolar plates. The stress exerted by gas bubbles is directly proportional to gas bubbles detachment diameter. In addition, the non-homogeneous distribution of gas bubbles can cause local water scarcity on the membrane and the catalyst, resulting in the formation of hotspots, which creates small areas with extremely high temperatures and increases the thermal stress acting on the membrane and the catalyst [81,98].

Increasing the ripple factor of the input power increases the power dissipated as heat energy due to the increase of the ripple current component. However, since the production of hydrogen depends on the direct current component, the rate of the electrolysis process remains unchanged. This increases the operating temperature, since the heat absorbed by the - endothermic - electrolysis reaction remains the same [90,99].

Zhang et al. [100] examined the effect of different loading waveforms on the dynamic response of a PEM electrolyzer and found that the temperature rise caused by a multi-stepped loading waveform was higher than that caused by single-stepped and linear loading waveforms, while a linear loading waveform caused a higher temperature increase than a single-stepped waveform. Zhang et al. suggested that the increase in temperature was caused by the increase in activation overvoltage losses. However, the ripple factor of the input waveforms as a possible cause of the temperature increase was not considered. The multi-stepped loading waveform had the highest ripple factor, followed by linear loading and the single-stepped waveform. The higher the ripple factor, the higher the alternating current which dissipates its energy in the form of heat without participation in the electrolysis reaction. Therefore, more research is needed to fully understand the effect of different input power waveforms on the degradation of PEM electrolyzers.

Finally, a lower water content and a higher temperature both decrease the chemical and mechanical stability of Perfluorosulfonic acid polymers [101,102]. However, input water flow rate and temperature can be controlled to overcome these issues. When the temperature increases, water can be fed either at lower temperatures or higher input flow rates than during normal operation to dissipate the heat accumulated in the electrolyzer.

4.2. Partial loading

Partial loading decreases the detachment diameter of gas bubbles which increases the area of the active layer of the catalyst exposed to the electrolysis reaction [81,103]. Besides, partial loading reduces the detachment of the anti-corrosion coating material and the corrosion of the PTL and the bipolar plates [82–84].

In contrast, partial loading accelerates the thinning of the membrane and the catalyst ionomer. When oxygen penetrates through the membrane from anode to cathode, it can react with hydrogen to produce hydrogen peroxide. Hydrogen peroxide is further involved in different reactions where hydroxyl radicals are formed via the Fenton reaction in the presence of metal ions. Hydroxyl radicals attack carboxylic acid end-groups in the membrane and the catalyst ionomer, causing their thinning. The source of metal ions is thought to be impurities in the water or the stainless steel used in the construction of the equipment [89,104].

Although oxygen permeability is directly proportional to the input current, the molar ratio of oxygen to hydrogen in cathode is low at higher currents, which decreases the formation of hydrogen peroxide. Therefore, membrane thinning is inversely proportional to the input current [51,105]. However, temperature has a larger impact on membrane thinning than input current. When the operating temperature increases from 60 °C to 80 °C, membrane thinning can accelerate up to 5 times [106].

Siracusano et al. [107] measured the degradation rate of a PEM electrolyzer at 1 A/cm^2 and 3 A/cm^2 with a catalyst loading of 1.27 mg$_{Ir+Ru}$/cm^2 for 1000 h. It was found that the degradation rate increased from 5 μV/h at 1 A/cm^2 to 11 μV/h at 1 A/cm^2. Siracusano et al. suggested that the increase in degradation is due to the changes in the roughness and the surface chemistry of the catalyst. Moreover, Siracusano et al. examined membrane thickness and found no clear evidence for membrane thinning. Besides, it was found that ohmic overvoltage losses decreased, which indicates a better ionic or electric conductivity. However, the tests were executed on a single cell, and the material of construction for the tubing was not reported. The absence of other potential electrolysis plant components and stainless steel pipes may highly decrease the concentration of metal ion impurities in the feed water. This in turn, slows down the Fenton reaction. Moreover, at a low concentration of metal ion impurities, the reduction in membrane thickness may be undetectable.

It seems that partial loading can initially improve the performance of a PEM electrolyzer and decrease ohmic overvoltage losses due to the increased ionic conductivity of a thinner membrane. However, it can also cause the thickness of the membrane to reach a critical value where the transport of hydrogen to the anode increases to unsafe levels. The potential severity of this issue will increase with the trend of reducing the thickness of the polymer electrolyte membrane to decrease capital costs. However, with the promising research results of using graphene with perfluorosulfonic acid polymers, as discussed in Section 2.3, the penetration of gaseous molecules through the membrane decreases, which reduces the membrane thinning due to partial loading and allows for capital costs saving because of the decreased thickness of the membrane.

4.3. On/off cycles

Another parameter that influences degradation during dynamic operation is switching between on and off modes. Weiß et al. [108] explained the effect of on/off times on degradation. During shutdown, hydrogen crosses from the cathode to the anode where it accumulates and lowers the anode catalyst potential. At a low enough voltage (about 0.8 V at 80 °C), hydrogen reduces the anode catalyst iridium oxide to elemental iridium metal. During operation, iridium is oxidized again into an amorphous structure instead of the original crystalline one. Although amorphous iridium oxide catalyst has a higher activity, it also exhibits a lower stability. This improves the performance initially, but leads to a quicker degradation, because of the increased dissolution rate of iridium. With the current state of the art in anode catalyst manufacturing, the effect of iridium dissolution is not critical [109,110]. However, when iridium loading will be decreased to reduce capital cost, and on/off cycles will increase to follow VRE production, the possibility of iridium dissolution being a limiting factor for the lifetime of PEM electrolyzers increases. Weiß et al. suggested keeping PEM electrolyzers in a stand-by mode at about 1% of input current to prevent the reduction of iridium oxide [108].

Rakousky et al. [17] studied the effect of dynamic operation on PEM electrolyzer degradation. It was found that dynamic operation with 6 h in on mode followed by 6 h in off mode for 1000 h decreased degradation. However, when the intervals became faster and more frequent (10 min), degradation worsened. This is in line with the findings of Weiß et al. where more frequent intervals increase degradation, although Rakousky et al. suggested that the degradation of the cathode catalyst is the main cause of increased electrolyzer degradation. In contrast, when Frensch et al. investigated the effect of dynamic operation, It was found that having shorter interval times of on and off modes decreases degradation [111]. However, Rakousky et al. did not report the operating pressure, while Frensch et al. performed their tests at atmospheric pressure. Increasing the differential pressure between the cathode and the anode increases hydrogen crossover which accelerates iridium dissolution. Furthermore, it is recommended to report the quality of the dc current used during electrolysis experiments, as it may also influence the degradation of the PEM electrolyzer, as discussed below in Section 4.4.

On/Off cycles are not expected to pose a significant challenge to off-grid systems where there is a direct connection between VRE sources and a PEM electrolyzer, because short-interval interruptions rarely occur in solar and wind power plants [112,113]. However, when connecting a PEM electrolyzer to an electricity grid with a high volatility due to the high share of VRE, the possibility of shutting down PEM electrolyzers for short-intervals during consumption peaks and low production periods increases, which accelerates their degradation. Therefore, the complete shutdown of PEM electrolyzers for short intervals during dynamic operation should be avoided as much as possible.

4.4. Input power quality

An electric power converter is an essential component of electrolyzer operation. AC-DC converters are needed for connecting PEM electrolyzers to the electricity grid or wind energy, while DC-DC converters are needed to connect to photovoltaics. Different power converters have different output waveforms, such as square wave, triangular wave, and sinusoidal wave, which all produce different current ripples [114]. Parache et al. [115] investigated the effect of current ripples on PEM electrolyzer degradation for 3000 h. It was found that overvoltage degradation increased about 5 times when a triangular current ripple with a frequency of 10 kHz is used instead of the reference constant current. However, degradation decreased by roughly 40% when a sinusoidal current ripple with a frequency of 300 Hz was used. The differences in degradation with different input power waveforms and frequencies can likely be attributed to differences in gas bubble accumulation and ripple current, as discussed in Section 4.1.

Parache et al. [115] suggested that the increase in overvoltage difference over time between the triangular waveform current and the reference constant current is due to the passivation of titanium on the anode side. However, the effect of the ripple factor, which increases the operating temperature, was not taken into account. The ripple factor of a triangular waveform with a frequency of 10 kHz is roughly 20% higher than that of the reference constant current. Consequently, more research is needed to elucidate the reasons behind changes in the

Table 2
The effect of operator actions during dynamic operation on the degradation of PEM electrolyzers. The (+) sign indicates a less degradation while the (–) sign indicates more degradation.

Actions	Effect	Reason	Component
Load fluctuation	– Reduce catalyst layer activity – Change porous structure of catalyst layer – Accelerate PTL and bipolar plate passivation – Accelerate membrane and catalyst ionomer thinning – Increase membrane and catalyst water starvation and hot spot formation	– Higher gas bubble accumulation – Higher ripple current (Higher temperature)	Membrane Catalyst layer PTL Bipolar plates
Partial load	+ Decrease catalyst active layer detachment + Decrease PTL and bipolar plates passivation – Accelerate membrane and catalyst ionomer thinning	+ Lower gas bubbles detachment diameter – Higher oxygen to hydrogen ratio in cathode	Membrane Catalyst layer PTL Bipolar plates
On/Off cycles	– Reduce catalyst layer activity	– Higher hydrogen gas accumulation in anode	Catalyst layer
Power quality	– Accelerate PTL and bipolar plates passivation – Accelerate membrane and catalyst ionomer thinning	– Input power waveform and frequency – Higher ripple current (Higher temperature)	Membrane Catalyst layer PTL Bipolar plates

degradation rate as a function of input power quality. In addition, reporting input current/voltage quality in different research is necessary to facilitate comparison between different studies. An undesirable side effect of increasing the quality of power converters used to minimize degradation and maximize efficiency, is the increase in costs. However, using more modern transistor-based power converters can decrease the PEM electrolyzer-specific energy consumption by up to 14% when compared with 6-pulse thyristor converters [99]. Therefore, the cost of power converters and the quality of their output waveform should be included in the optimization of PEM electrolyzer operation.

Table 2 summarizes how different actions taken during dynamic operation by the operator/optimizer affects degradation, and which electrolyzer component is affected. The (+) sign indicates a positive effect on degradation (less degradation) while the (−) sign indicates the opposite (more degradation). As can be seen in Table 2, load fluctuation has the highest impact on the degradation of a PEM electrolyzer. Increasing load fluctuation increases both gas bubble accumulation and the ripple current, which increases the degradation of all electrolyzer components. Metal ions in the feed-in water, whether from water impurities or stainless steel used in equipment manufacturing, should be avoided as much as possible. Most of the actions taken during the dynamic operation of a PEM elctrolyzer, except for switching between on and off modes, accelerate the thinning of the membrane and the catalyst ionomer in the presence of metal ions.

5. Dynamic PEM electrolyzer operation and the market

The dynamic operation of a PEM electrolyzer can influence the cost of green hydrogen in various ways. Operating PEM electrolyzers when electricity prices are low and VRE sources are available decreases the operational expenses. In addition, when PEM electrolyzers are used for balancing the electricity grid, the reserve market can provide extra revenues to the operation, thus decreasing the levelized cost of the green hydrogen produced. Conversely, lowering the number of operating hours, when compared with constant operation, increases the levelized cost due to the resulting higher contribution of capital costs. Table 3 summarizes the influence of PEM electrolyzer mode of operation on electricity prices, operating hours, and revenues from the reserve market which are affecting the levelized cost of the produced green hydrogen.

Table 3
Effect of proton exchange membrane electrolyzer mode of operation on electricity prices, operating hours, and revenues from the reserve market.

	Constant operation	Dynamic operation
Electricity prices	↑	↓
Operating hours	↑	↓
Reserve market revenue	↓	↑

Currently, global hydrogen demand is about 90 Mt/year and it is expected to rise in the future [116]. In IRENA's scenario for limiting global warming to 1.5 °C by 2100, clean hydrogen production in 2030 reaches 154 Mt [12]. In 2022, Water electrolysis accounted for roughly 5% of global hydrogen production, while the fossil-based route accounted for the other 95%, out of which only 8 Mt is produced at sites with carbon capture and storage facilities. Det Norske Veritas forecasts that in 2030, 18% of hydrogen production will come from water electrolysis. Currently, the two largest hydrogen consumers are petroleum refining and the production of ammonia for fertilizers. However, it is expected that a significant demand for hydrogen as an energy carrier will arise, both for direct utilization and for producing various e-fuels. Moreover, the demand for hydrogen as an energy carrier is expected to exceed its demand for non-energy applications after 2040 [116]. One of the major challenges facing green hydrogen production is its high cost, as the price of green hydrogen is currently 2 to 3 times higher than hydrogen produced by steam methane reforming [117].

The causes of this high cost can be partially attributed to the high cost of PEM electrolyzers. This can be divided into the electrolyzer stack costs and balance of plant costs. The PEM electrolyzer stack accounts for roughly 45% of the total cost. IRENA forecasts that the stack cost of PEM electrolyzers can be reduced from 400 USD/kW in 2020 to less than 100 USD/kW in 2050. This reduction will be facilitated by the development of cheaper materials for the manufacturing of PEM electrolyzers, e.g. through the replacement of expensive noble metals in catalysts and other components. In addition, the learning curve associated with producing PEM electrolyzers on a large scale will decrease the overall cost, including balance of plant costs [16].

However, reducing the cost of the electrolyzer alone is not enough for economically viable green hydrogen. The cost and consumption of electricity in the electrolyzer also needs to be reduced, since electricity price is the single main parameter affecting the levelized cost of green hydrogen [118,119]. IRENA forecasts that, in the long run, decreasing electricity cost, reducing the amount of expensive materials used and switching to affordable materials as much as possible, benefiting from the economy of scale, and the learning curve in manufacturing can reduce green hydrogen cost by 85% [16].

5.1. Electricity purchase

According to the directive act adopted by the European Commission in February 2023 regarding the production of renewable liquid- and gaseous transport fuels of non-biological origin, hydrogen produced by electrolyzers can be classified as green (renewable) only if the electricity used can be proven to be renewable according to temporal and geographical correlations [120]. This can be done by directly connecting the electrolysis plant to a renewable power plant or by establishing power purchase agreements with such plants.

Moradpoor et al. [121] investigated different scenarios for purchasing renewable electricity in Finland and examined their effect on the break-even price of the green hydrogen produced. When using a PEM electrolyzer, It was found that the break-even price of green hydrogen ranged from about 4.75 EUR/kg H_2 in the case of buying baseload using power purchase agreement contracts, to about 6.14 EUR/kg H_2 on a pay as produced power purchase agreement contract with the electricity grid as the balancing agent and compressed air energy storage for decreasing dependency on the electricity grid. When the PEM electrolysis plant was directly connected to a wind park with the electricity grid as a balancing agent, the break-even price of produced hydrogen was 6 EUR/kg H_2.

However, both in the direct connection and the pay as produced power purchase agreement contract scenarios a situation can arise when the wind energy available is not enough to operate the PEM electrolyzer at full power. In such a case, if the grid is used for balancing, all electricity supplied by the grid should be proven to be renewable on a monthly basis until the end of 2029 and on a hourly basis from the beginning of 2030 in order to classify the produced hydrogen as green [120]. If proving the renewable origin of electricity is not possible, decreasing the electrolysis capacity factor or adding more electricity storage is needed. This will increase the break-even price of green hydrogen even further.

In addition, Ginsberg et al. [122] compared the levelized cost of hydrogen produced by a PEM electrolyzer in constant and dynamic operation. Electricity production profile of California in 2019 was used, which had a 14% share of solar energy and 7% of wind energy with an average electricity price of 0.03 USD/kWh. It was found that the price of green hydrogen decreases with dynamic operation by roughly 9.5% when compared to constant operation. However, Ginsberg et al. did not consider the possible revenues from the electricity reserve market which can increase the green hydrogen price saving. In addition, it is expected that more VRE sources connected to the electricity grid will increase its volatility, which will reduce the cost of green hydrogen even further. In 2021, renewables accounted for 34.8% of California total electricity production [123]. Renewable energies considered in this figure include solar, wind, biomass, small hydro, and geothermal energy. California targets a 60% share of renewables in all retail sales by 2030 [124]. If realized, these plans will increase the advantage of dynamic operation over constant operation.

5.2. Electricity reserve market

The electricity reserve market increases the reliability of the electricity grid by balancing the production and the consumption of electricity. As the share of VRE in the electricity grid increases, the volatility of the grid increases. Therefore, more reserve is needed for ensuring its reliability. One way to increase the reliability of the electricity grid is to increase the electricity grid flexibility by demand response. Dynamic operation of PEM electrolyzers can provide the electricity grid with part of this flexibility needed to ensure the reliability of the grid.

Bertuccioli et al. [31] modeled the influence of reserve market revenues in Germany 2030 on the levelized cost of green hydrogen. It was found that the benefits from reserve market revenues and improving efficiency outweigh the increase in capital cost. Bertuccioli et al. forecasted that green hydrogen cost can be reduced by approximately 45% when the electrolyzer is operating at 50% of its capacity, offering both positive and negative power balancing capabilities to the grid. However, it was assumed that the degradation rate is identical during constant and dynamic operation. The accelerated degradation caused by dynamic operation will reduce both the hydrogen output and the lifetime of the PEM electrolyzer. This consideration will increase the levelized cost of green hydrogen and affect the economic evaluations conducted in both studies.

As can be seen throughout this critical review, different actions and parameters during the dynamic operation of PEM electrolysis have contradictory effects on the levelized cost of the produced green hydrogen. Therefore a holistic optimization approach is needed, to ensure the reduction of green hydrogen cost. Fig. 4 shows some interconnected parameters to be taken into account while optimizing the dynamic operation of a PEM electrolyzer. These parameters can increase or decrease depending on the market where the PEM electrolyzer is being operated. Dynamic operation can reduce the levelized cost of green hydrogen by utilizing cheap renewable electricity and revenues from the electricity reserve market. In off-grid VRE systems and for ensuring the renewable origin of the electricity used in on-grid systems, the additional cost of an on-site energy storage system, which increases the capacity factor of the electrolyzer, should also be considered in the optimization process. Moreover, actions taken by operator and adjustments of the operating parameters affect the degradation, efficiency, capacity factor, and operational safety limits of the electrolyzer.

Finally, PEM electrolyzer stack development should consider the operational mode in which the electrolyzer will be used. Furthermore, improvements of PEM electrolyzers should be compared with the state-of-the-art in both constant and dynamic operation modes using different sets of criteria with different weights for each criterion. For example, the lowest partial loading allowed or the rate of change of input current is more important in dynamic operation than in constant operation. The current research trend of reducing iridium loading in the anode electrocatalyst or reducing the thickness of the polymer electrolyte membrane decreases the manufacturing capital costs, but at the same time it affects the degradation of the electrolyzer differently in constant and dynamic operation. In addition, a thinner polymer electrolyte membrane reduces the capability of the electrolyzer to follow the production of VRE at times of low production, especially at elevated cathode–anode pressure differences. Moreover, increasing capital costs in balance of plant, such as installing mechanical compressors and modern power converters, can slow electrolyzer degradation, and have a beneficial effect on electrolyzer efficiency and safety limits. Therefore, capital costs associated with manufacturing the electrolyzer, possible reduction of manufacturing capital costs at the expense of increasing the degradation, and the capital costs of the balance of plant should all be included in the optimization of the levelized cost of green hydrogen during the dynamic operation of a PEM electrolyzer.

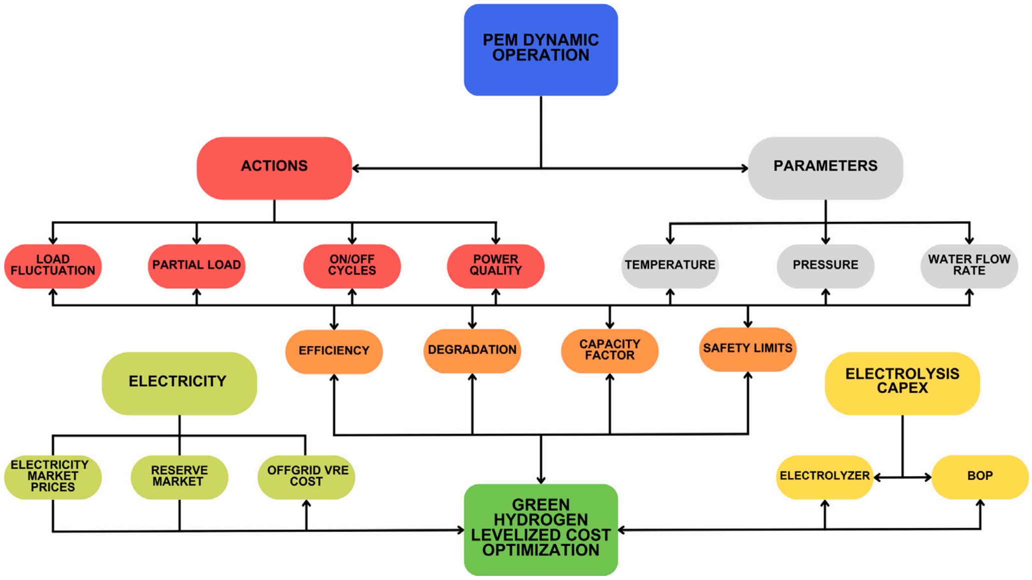

Fig. 4. Actions and parameters to be considered during the optimization of the levelized cost of green hydrogen produced during the dynamic operation of a PEM electrolyzer.

6. Conclusion

PEM electrolyzers are a good candidate for utilizing VRE production via dynamic operation. PEM electrolyzers have a fast response time, a high input current density, and a wide operating range. Optimizing the levelized cost of green hydrogen while utilizing cheap renewable electricity is a complicated task due to the large number of interconnected variables that must be considered. Different actions taken by the operator/optimizer, operating parameters, electrolyzer capital costs, and electricity costs all affect each other and affect the levelized cost of the green hydrogen produced. The conclusions regarding the different actions taken by the operator during the dynamic operation of a PEM electrolyzer are summarized briefly below.

Load fluctuation is associated with the utilization of cheaper renewable electricity. However, it decreases the capacity factor of operation, increases the operating temperature, and worsens the efficiency and degradation of a PEM electrolyzer. Partial loading, at atmospheric pressure, improves the efficiency of PEM electrolyzers. On the other hand, it has both positive and negative effects on degradation. Partial loading decreases the detachment of the catalyst active layer and the passivation of the PTL and the bipolar plates, while increasing the thinning of the membrane and the catalyst ionomer. Moreover, partial loading at a balanced supply enables a PEM electrolyzer operator to benefit from positive and negative balancing revenues from the reserve market by decreasing consumption when not enough supply is available and increasing consumption when extra supply is available. However, this comes at the expenses of a reduced capacity factor.

Frequent on/off cycles expedite the dissolution of iridium, which decreases the activity of the anode catalyst and reduces the performance of the electrolyzer over time, especially if the catalyst loading was reduced to save manufacturing costs. Therefore, keeping a PEM electrolyzer on stand-by at about 1% of rated input current can reduce degradation when on/off cycles are needed. However, this improvement in degradation is won at the expense of higher electricity consumption compared to completely shutting down the electrolyzer. The power quality of the input current/voltage through power converters also affects degradation and efficiency. Power converters with higher power quality increase balance of plant costs. However, more research is needed to elucidate the reasons behind the influence of input power waveform, frequency, and current ripples the degradation and efficiency of PEM electrolyzers.

Overall, to reduce the levelized cost of green hydrogen, a holistic optimization of PEM electrolyzer dynamic operation must be undertaken. Such an optimization exercise has to consider all interconnected variables in the market where the PEM electrolyzer is being operated. The authors anticipate that data driven approaches, such as Machine Learning and Digital Twins, will play a key role in achieving optimized dynamic PEM electrolysis processes for affordable green hydrogen.

Finally, the dynamic operation of PEM electrolyzers affects and is affected by various policies. In the electricity reserve market, the calculation method of the size of the minimum bid capacity can influence the optimization of the dynamic operation. If the reserve market solely calculates the size of the minimum bid using single unit capacity, this can disqualify some PEM electrolysis plants from participating in the reserve market and reduce their economic viability. However, if the aggregated capacity of several units can be used in calculating the size of the minimum bid, this will qualify more PEM electrolysis plants to exploit the electricity reserve market, since a PEM electrolysis plant usually consists of several PEM electrolyzer stacks and each stack is a single reserve unit. In addition, the time basis for proving the renewable origin of electricity for the purposes of classifying the produced hydrogen as renewable will affect the optimization of dynamic operation. In the European Union, until the end of 2029, a monthly basis will be used which gives more room for the optimization algorithm to reduce the levelized cost of the produced green hydrogen. However, starting from the beginning of 2030, an hourly basis will be used which will tighten the constraints on the optimization algorithm.

Ultimately, dynamic operation of PEM electrolyzers can help the energy sector achieve carbon neutrality targets. Dynamic operation follows the production of VRE, which improves the integration of VRE into the electricity grid. In addition, dynamic operation improves the stability of the electricity grid by utilizing the demand response capabilities of PEM electrolyzers. Furthermore, dynamic operation decouples the increase in VRE from increasing electricity storage capacity by utilizing VRE to directly produce a product (green hydrogen) instead of storing electricity. Therefore, a higher percentage of VRE can be permitted without disrupting the electricity grid. In addition, optimizing the dynamic operation of PEM electrolyzers can lower the cost of green hydrogen production, improving its economic viability. Furthermore, increasing hydrogen production at lower electricity prices and decreasing hydrogen production at higher electricity prices stabilizes the levelized cost of green hydrogen against unexpectedly high electricity prices, which increases the robustness of PEM electrolysis operation. All these implications can accelerate the carbon neutrality transition in energy sector.

CRediT authorship contribution statement

H. Sayed-Ahmed: Conceptualization, Methodology, Validation, Visualization, Writing – original draft. **Á.I. Toldy:** Validation, Writing – review & editing. **A. Santasalo-Aarnio:** Conceptualization, Validation, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare no conflict of interest.

Data availability

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

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References

[1] Ritchie H, Roser M, Rosado P. CO2 and greenhouse gas emissions. Our World Data 2020. [Online]. Available: https://ourworldindata.org/co2-and-greenhouse-gas-emissions.

[2] Climate Watch. Historical GHG emissions. 2022, Online, accessed 31-03-2023. [Online]. Available: https://www.climatewatchdata.org/ghg-emissions.

[3] Lund PD, Lindgren J, Mikkola J, Salpakari J. Review of energy system flexibility measures to enable high levels of variable renewable electricity. Renew Sustain Energy Rev 2015;45:785–807.

[4] Auer S. The stability and control of power grids with high renewable energy share (Ph.D. dissertation), Humboldt-Universität zu Berlin; 2018.

[5] Xu T, Gao W, Qian F, Li Y. The implementation limitation of variable renewable energies and its impacts on the public power grid. Energy 2022;239:121992.

[6] Martins F, Moura P, de Almeida AT. The role of electrification in the decarbonization of the energy sector in Portugal. Energies 2022;15(5):1759.

[7] Gray N, McDonagh S, O'Shea R, Smyth B, Murphy JD. Decarbonising ships, planes and trucks: An analysis of suitable low-carbon fuels for the maritime, aviation and haulage sectors. Adv Appl Energy 2021;1:100008.

[8] Skov IR, Schneider N. Incentive structures for power-to-X and e-fuel pathways for transport in EU and member states. Energy Policy 2022;168:113121.

[9] Burre J, Bongartz D, Brée L, Roh K, Mitsos A. Power-to-X: Between electricity storage, e-production, and demand side management. Chem Ing Tech 2019;92:74–84.

[10] Kountouris I, Langer L, Bramstoft R, Münster M, Keles D. Power-to-X in energy hubs: A Danish case study of renewable fuel production. Energy Policy 2023;175:113439.

[11] Ueckerdt F, Bauer C, Dirnaichner A, Everall J, Sacchi R, Luderer G. Potential and risks of hydrogen-based e-fuels in climate change mitigation. Nature Clim Change 2021;11:1–10.

[12] International Renewable Energy Agency. World energy transitions outlook 2022: 1.5 C pathway. Tech. Rep., Abu Dhabi: International Renewable Energy Agency; 2022, [Online]. Available: https://www.irena.org/publications/2022/mar/world-energy-transitions-outlook-2022.

[13] Mohanpurkar M, Luo Y, Terlip D, Dias F, Harrison K, Eichman J, Hovsapian R, Kurtz J. Electrolyzers enhancing flexibility in electric grids. Energies 2017;10:1836.

[14] Allidières L, Brisse A, Millet P, Valentin S, Zeller M. On the ability of pem water electrolysers to provide power grid services. Int J Hydrogen Energy 2019;44(20):9690–700, 9th International Conference on Hydrogen Production (ICH2P-2018).

[15] Department for Business, Energy & Industrial Strategy. Hydrogen production costs 2021. Tech. Rep., United Kingdom: Department for Business, Energy & Industrial Strategy; 2021, p. 1–36, [Online]. Available: https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/1011506/Hydrogen_Production_Costs_2021.pdf.

[16] International Renewable Energy Agency. Green hydrogen cost reduction: Scaling up electrolysers to meet the 1.5 C climate goal. Tech. Rep., Abu Dhabi: International Renewable Energy Agency; 2020, [Online]. Available: https://www.irena.org/publications/2020/Dec/Green-hydrogen-cost-reduction.

[17] Rakousky C, Reimer U, Wippermann K, Kuhri S, Carmo M, Lueke W, Stolten D. Polymer electrolyte membrane water electrolysis: Restraining degradation in the presence of fluctuating power. J Power Sources 2017;342:38–47.

[18] Kojima H, Nagasawa K, Todoroki N, Ito Y, Matsui T, Nakajima R. Influence of renewable energy power fluctuations on water electrolysis for green hydrogen production. Int J Hydrogen Energy 2023;48(12):4572–93.

[19] Guilbert D, Papakonstantinou G. Modeling, degradation study, failures diagnosis and faulty operating management of electrolyzers. Membranes 2022;12(12).

[20] Santasalo-Aarnio A, Virtanen J, Gasik M. SO2 carry-over and sulphur formation in a SO2-depolarized electrolyser. J Solid State Electrochem 2016;20:1655–63.

[21] Steimke J, Steeper T, Colon-Mercado H, Gorensek M. Development and testing of a PEM SO2-depolarized electrolyzer and an operating method that prevents sulfur accumulation. Int J Hydrogen Energy 2015;40.

[22] Krüger AJ, Krieg HM, Grigoriev SA, Bessarabov D. Various operating methods and parameters for SO2 electrolysis. Energy Sci Eng 2015;3(5):468–80.

[23] Buttler A, Spliethoff H. Current status of water electrolysis for energy storage, grid balancing and sector coupling via power-to-gas and power-to-liquids: A review. Renew Sustain Energy Rev 2018;82:2440–54.

[24] Lehner M, Tichler R, Steinmüller H, Koppe M. Water electrolysis. In: Power-to-gas: Technology and business models. Cham: Springer International Publishing; 2014, p. 19–39.

[25] Web Of Science™. Web of science core collection. 2023, Online, accessed 09-03-2023. [Online]. Available: https://www.webofscience.com/wos/woscc/basic-search.

[26] Rashid M, Al Mesfer M, Naseem H, Danish M. Hydrogen production by water electrolysis: A review of alkaline water electrolysis, PEM water electrolysis and high temperature water electrolysis. Int J Eng Adv Technol 2015;ISSN:2249–8958, [Online]. Available: https://www.researchgate.net/publication/273125977_Hydrogen_Production_by_Water_Electrolysis_A_Review_of_Alkaline_Water_Electrolysis_PEM_Water_Electrolysis_and_High_Temperature_Water_Electrolysis.

[27] Shiva Kumar S, Himabindu V. Hydrogen production by PEM water electrolysis – A review. Mater Sci Energy Technol 2019;2(3):442–54.

[28] Carmo M, Fritz DL, Mergel J, Stolten D. A comprehensive review on PEM water electrolysis. Int J Hydrogen Energy 2013;38(12):4901–34.

[29] Schmidt Rivera XC, Topriska E, Kolokotroni M, Azapagic A. Environmental sustainability of renewable hydrogen in comparison with conventional cooking fuels. J Clean Prod 2018;196:863–79.

[30] Tenhumberg N, Büker K. Ecological and economic evaluation of hydrogen production by different water electrolysis technologies. Chem Ing Tech 2020;92(10):1586–95.

[31] Bertuccioli L, Chan A, Hart D, Lehner F, Madden B, Standen E. Study on development of water electrolysis in the EU - Final Report. In: Fuel cells and hydrogen joint undertaking. Tech. Rep. February, E4tech Sàrl with Element Energy Ltd for the Fuel Cells and Hydrogen Joint Undertaking; 2014, p. 83.

[32] Toghyani S, Fakhradini S, Afshari E, Baniasadi E, Abdollahzadeh Jamalabadi MY, Safdari Shadloo M. Optimization of operating parameters of a polymer exchange membrane electrolyzer. Int J Hydrogen Energy 2019;44(13):6403–14.

[33] Stiber S, Hehemann M, Carmo M, Müller M, Ayers K, Capuano C, Danilovic N, Morawietz T, Biswas I, Gazdzicki P, Heger J-F, Gago A, Friedrich K. Long-term operation of nb-coated stainless steel bipolar plates for proton exchange membrane water electrolyzers. Adv Energy Sustain Res 2022;3:2200024.

[34] Plevová M, Hnát J, Bouzek K. Electrocatalysts for the oxygen evolution reaction in alkaline and neutral media. A comparative review. J Power Sources 2021;507:230072.

[35] Ahmed KW, Jang MJ, Park MG, Chen Z, Fowler M. Effect of components and operating conditions on the performance of PEM electrolyzers: A review. Electrochem 2022;3(4):581–612.

[36] BullionByPost. The most expensive metal. 2022, Online, accessed 30-12-2022. [Online]. Available: https://www.bullionbypost.eu/index/precious-metal-market/most-expensive-metal/.

[37] Minke C, Suermann M, Bensmann B, Hanke-Rauschenbach R. Is iridium demand a potential bottleneck in the realization of large-scale PEM water electrolysis? Int J Hydrogen Energy 2021;46(46):23581–90.

[38] Cowley A, Jiang J, Tang B, Wang A, Bloxham L, Brown S, Cole L, Fujita M, Girardot N, Raithatha R, Ryan M. PGM market report. Tech. Rep., Johnson Matthey; 2022, [Online]. Available: https://matthey.com/documents/161599/509428/PGM-market-report-May-2022.pdf/542bcada-f4ac-a673-5f95-ad1bbfca5106?t=1655877358676.

[39] Kiemel S, Smolinka T, Lehner F, Full J, Sauer A, Miehe R. Critical materials for water electrolysers at the example of the energy transition in Germany. Int J Energy Res 2021;45(7):9914–35.

[40] Hydrogen Council, McKinsey & Company. Hydrogen for Net-Zero: A critical cost-competitive energy vector. Tech. Rep., Hydrogen Council, McKinsey & Company; 2021, [Online]. Available: https://hydrogencouncil.com/wp-content/uploads/2021/11/Hydrogen-for-Net-Zero.pdf.

[41] Zhang K, Liang X, Wang L, Sun K, Wang Y, Xie Z, Wu Q, Bai X, Hamdy MS, Chen H, Zou X. Status and perspectives of key materials for PEM electrolyzer. Nano Res Energy 2022;1:e9120032.

[42] Gao J, Tao H, Liu B. Progress of nonprecious-metal-based electrocatalysts for oxygen evolution in acidic media. Adv Mater 2021;33.

[43] Patel P, Datta M, Velikokhatnyi O, Kuruba R, Damodaran K, Jampani P, Gattu B, Shanthi P, Damle S, Kumta P. Noble metal-free bifunctional oxygen evolution and oxygen reduction acidic media electro-catalysts. Sci Rep 2016;6:28367.

[44] Grigoriev S, Millet P, Volobuev S, Fateev V. Optimization of porous current collectors for PEM water electrolysers. Int J Hydrogen Energy 2009;34(11):4968–73, 2nd International Workshop on Hydrogen.

[45] Doan L, Lee H, Shah SSH, Kim M, Kim C-H, Cho H-S, Kim T. A review of the porous transport layer in polymer electrolyte membrane water electrolysis. Int J Energy Res 2021;45.

[46] Ďurovič M, Hnát J, Bouzek K. Electrocatalysts for the hydrogen evolution reaction in alkaline and neutral media. A comparative review. J Power Sources 2021;493:229708.

[47] Eftekhari A. Electrocatalysts for hydrogen evolution reaction. Int J Hydrogen Energy 2017;42(16):11053–77.

[48] Guo F, Macdonald TJ, Sobrido AJ, Liu L, Feng J, He G. Recent advances in ultralow-pt-loading electrocatalysts for the efficient hydrogen evolution. Adv Sci 2023.

[49] Hagelüken C. Recycling the platinum group metals: A European perspective. Platinum Met Rev 2012;56:29–35.

[50] Ito H, Miyazaki N, Ishida M, Nakano A. Cross-permeation and consumption of hydrogen during proton exchange membrane electrolysis. Int J Hydrogen Energy 2016;41(45):20439–46.

[51] Frensch SH, Serre G, Fouda-Onana F, Jensen HC, Christensen ML, Araya SS, Kær SK. Impact of iron and hydrogen peroxide on membrane degradation for polymer electrolyte membrane water electrolysis: Computational and experimental investigation on fluoride emission. J Power Sources 2019;420:54–62.

[52] Tjarks G, Mergel J, Stolten D. Dynamic operation of electrolyzers - systems design and operating strategies. In: Hydrogen science and engineering: Materials, processes, systems and technology. Wiley-VCH Verlag GmbH & Co. KGaA; 2016, p. 309–30.

[53] Speight JG. Chapter 12 - Fouling during hydrotreating. In: Speight JG, editor. Fouling in refineries. Boston: Gulf Professional Publishing; 2015, p. 303–28.

[54] Nyári J, Magdeldin M, Larmi M, Järvinen M, Santasalo-Aarnio A. Techno-economic barriers of an industrial-scale methanol CCU-plant. J CO2 Util 2020;39:101166.

[55] Bhattacharya S, Biswas S, Kulkarni A, Giddey S, Nguyen MNL. A review on synthesis of methane as a pathway for renewable energy storage with a focus on solid oxide electrolytic cell-based processes. Front Energy Res 2020;8.

[56] Ayers K, Dalton L, Anderson E. (Invited) efficient generation of high energy density fuel from water. Electrochem Soc Trans 2012;41:27–38.

[57] Trinke P, Bensmann B, Reichstein S, Hanke-Rauschenbach R, Sundmacher K. Hydrogen permeation in PEM electrolyzer cells operated at asymmetric pressure conditions. J Electrochem Soc 2016;163(11):F3164.

[58] Bukola S, Creager S. Graphene-based proton transmission and hydrogen crossover mitigation in electrochemical hydrogen pump cells. Electrochem Soc Trans 2019;92:439–44.

[59] Ion-Ebrasu D, Pollet B, Spinu-Zaulet A, Soare A, Carcadea E, Varlam M, Caprarescu S. Graphene modified fluorinated cation-exchange membranes for proton exchange membrane water electrolysis. Int J Hydrogen Energy 2019;44.

[60] Pham C-T, Månsson D. On the physical system modelling of energy storages as equivalent circuits with parameter description for variable load demand (Part I). J Energy Storage 2017;13:73–84.

[61] Lukács Z, Kristóf T. A generalized model of the equivalent circuits in the electrochemical impedance spectroscopy. Electrochim Acta 2020;363:137199.

[62] Yodwong B, Guilbert D, PHATTANASAK M, Kaewmanee W, Hinaje M, Vitale G. Proton exchange membrane electrolyzer modeling for power electronics control: A short review. C 2020;6.

[63] Alexander CK, Sadiku MNO. Fundamentals of electric circuits. 4th ed.. New York: McGraw-Hill; 2009.

[64] Colbertaldo P, Gómez Aláez SL, Campanari S. Zero-dimensional dynamic modeling of PEM electrolyzers. Energy Procedia 2017;142:1468–73.

[65] García-Valverde R, Espinosa N, Urbina A. Simple PEM water electrolyser model and experimental validation. Int J Hydrogen Energy 2012;37(2):1927–38, 10th International Conference on Clean Energy 2010.

[66] Hernández-Gómez A, Ramirez V, Guilbert D. Investigation of PEM electrolyzer modeling: Electrical domain, efficiency, and specific energy consumption. Int J Hydrogen Energy 2020;45(29):14625–39.

[67] Bernt M, Schröter J, Möckl M, Gasteiger HA. Analysis of gas permeation phenomena in a PEM water electrolyzer operated at high pressure and high current density. J Electrochem Soc 2020;167(12):124502.

[68] Görgün H. Dynamic modelling of a proton exchange membrane (PEM) electrolyzer. Int J Hydrogen Energy 2006;31(1):29–38.

[69] Abdin Z, Webb C, Gray E. Modelling and simulation of a proton exchange membrane (PEM) electrolyser cell. Int J Hydrogen Energy 2015;40(39):13243–57.

[70] Selman JR, Tobias CW. Mass-transfer measurements by the limiting-current technique. In: Drew TB, Cokelet GR, Hoopes JW, Vermeulen T, editors. Advances in chemical engineering, Vol. 10. Academic Press; 1978, p. 211–318.

[71] Yodwong B, Guilbert D, Hinaje M, Phattanasak M, Kaewmanee W, Vitale G. Proton exchange membrane electrolyzer emulator for power electronics testing applications. Processes 2021;9(3).

[72] Guilbert D, Sorbera D, Vitale G. A stacked interleaved DC-DC buck converter for proton exchange membrane electrolyzer applications: Design and experimental validation. Int J Hydrogen Energy 2020;45(1):64–79.

[73] Guilbert D, Vitale G. Experimental validation of an equivalent dynamic electrical model for a proton exchange membrane electrolyzer. In: 2018 IEEE international conference on environment and electrical engineering and 2018 IEEE industrial and commercial power systems europe. 2018.

[74] Dang J, Yang F, Li Y, Deng X, Ouyang M. Transient behaviors and mathematical model of proton exchange membrane electrolyzer. J Power Sources 2022;542:231757.

[75] Yodwong B, Guilbert D, PHATTANASAK M, Kaewmanee W, Hinaje M, Vitale G. AC-DC converters for electrolyzer applications: State of the art and future challenges. Electronics 2020;9:912.

[76] Azam A, Li N, Zulkefli N, Masdar M, Majlan EH, Baharuddin NA, Zainoodin A, Mohamad Yunus R, Shamsul N, Husaini T, Shaffee A. Parametric study and electrocatalyst of polymer electrolyte membrane (PEM) electrolysis performance. Polymers 2023;15:560.

[77] Yodwong B, Guilbert D, Phattanasak M, Kaewmanee W, Hinaje M, Vitale G. Faraday's efficiency modeling of a proton exchange membrane electrolyzer based on experimental data. Energies 2020;13(18).

[78] Yigit T, Selamet OF. Mathematical modeling and dynamic Simulink simulation of high-pressure PEM electrolyzer system. Int J Hydrogen Energy 2016;41(32):13901–14.

[79] Trinke P, Bensmann B, Hanke-Rauschenbach R. Current density effect on hydrogen permeation in PEM water electrolyzers. Int J Hydrogen Energy 2017;42(21):14355–66.

[80] Atlam O, Kolhe M. Equivalent electrical model for a proton exchange membrane (PEM) electrolyser. Energy Convers Manage 2011;52(8):2952–7.

[81] Yuan S, Zhao C, Cai X, An L, Shen s, Yan X, Junliang Z. Bubble evolution and transport in PEM water electrolysis: Mechanism, impact, and management. Prog Energy Combust Sci 2023;96:101075.

[82] Prestat M. Corrosion of structural components of proton exchange membrane water electrolyzer anodes: A review. J Power Sources 2023;556:232469.

[83] Rakousky C, Keeley G, Wippermann K, Carmo M, Stolten D. The stability challenge on the pathway to high-current-density polymer electrolyte membrane water electrolyzers. Electrochim Acta 2018;278.

[84] Rakousky C, Reimer U, Wippermann K, Carmo M, Lueke W, Stolten D. An analysis of degradation phenomena in polymer electrolyte membrane water electrolysis. J Power Sources 2016;326:120–8.

[85] Barbir F. PEM electrolysis for production of hydrogen from renewable energy sources. Sol Energy 2005;78(5):661–9.

[86] Lee C, Lee J, Zhao B, Fahy K, Bazylak A. Transient gas distribution in porous transport layers of polymer electrolyte membrane electrolyzers. J Electrochem Soc 2020;167:024508.

[87] Angulo A, van der Linde P, Gardeniers H, Modestino M, Fernández Rivas D. Influence of bubbles on the energy conversion efficiency of electrochemical reactors. Joule 2020;4(3):555–79.

[88] Dukovic J, Tobias CW. The influence of attached bubbles on potential drop and current distribution at gas-evolving electrodes. J Electrochem Soc 1987;134(2):331.

[89] Frensch S. Lifetime investigation of PEM electrolyzers under realistic load profiles (Ph.D. dissertation), Ph.d.-serien for det ingeniør- og naturvidenskabelige fakultet, Aalborg Universitet, Aalborg Universitet; 2018, PhD supervisors: Prof. Søren Knudsen Kær, Aalborg Universitet Assoc. Prof. Samuel Simon Araya, Aalborg Universitet.

[90] Buitendach HP, Gouws R, Martinson CA, Minnaar C, Bessarabov D. Effect of a ripple current on the efficiency of a PEM electrolyser. Results Eng 2021;10:100216.

[91] Masoum MA, Fuchs EF. Chapter 1 - Introduction to power quality. In: Masoum MA, Fuchs EF, editors. Power quality in power systems and electrical machines (second edition). 2nd ed.. Boston: Academic Press; 2015, p. 1–104.

[92] Lettenmeier P. Efficiency - Electrolysis [White paper]. Tech. Rep., Siemens Energy; 2021, [Online]. Available: https://assets.siemens-energy.com/siemens/assets/api/uuid:a33a8c39-b694-4d91-a0b5-4d8c9464e96c/efficiency-white-paper.pdf.

[93] Scheepers F, Stähler M, Stähler A, Rauls E, Müller M, Carmo M, Lehnert W. Improving the efficiency of PEM electrolyzers through membrane-specific pressure optimization. Energies 2020;13(3).

[94] Frensch S, Olesen A, Simon Araya S, Kær S. Model-supported analysis of degradation phenomena of a PEM water electrolysis cell under dynamic operation. Electrochem Soc Trans 2018;85:37–45.

[95] Zhang H, Yuan T. Optimization and economic evaluation of a PEM electrolysis system considering its degradation in variable-power operations. Appl Energy 2022;324:119760.

[96] Bystron T, Veselý M, Paidar M, Papakonstantinou G, Sundmacher K, Bensmann B, Hanke-Rauschenbach R, Bouzek K. Enhancing PEM water electrolysis efficiency by reducing the extent of Ti gas diffusion layer passivation. J Appl Electrochem 2018;48.

[97] Babic U, Suermann M, Büchi FN, Gubler L, Schmidt TJ. Critical review—Identifying critical gaps for polymer electrolyte water electrolysis development. J Electrochem Soc 2017;164(4):F387.

[98] Lee JK, Lee C, Fahy KF, Zhao B, LaManna JM, Baltic E, Jacobson DL, Hussey DS, Bazylak A. Critical current density as a performance indicator for gas-evolving electrochemical devices. Cell Rep Phys Sci 2020;1(8):100147.

[99] Koponen J, Ruuskanen V, Hehemann M, Rauls E, Kosonen A, Ahola J, Stolten D. Effect of power quality on the design of proton exchange membrane water electrolysis systems. Appl Energy 2020;279:115791.

[100] Zhang X, Wang B, Xu Y, Wu L, Zhang F, He S, Zhang X, Jiao K. Effects of different loading strategies on the dynamic response and multi-physics fields distribution of PEMEC stack. Fuel 2023;332:126090.

[101] Millet P, Ranjbari A, Guglielmo F, Grigoriev S, Auprêtre F. Cell failure mechanisms in PEM water electrolyzers. Int J Hydrogen Energy 2012;37:17478–87.

[102] Sethuraman V, Weidner J, Haug A, Protsailo L. Durability of perfluorosulfonic acid and hydrocarbon membranes: Effect of humidity and temperature. J Electrochem Soc 2008;155.

[103] Leonard E, Shum AD, Normile S, Sabarirajan DC, Yared DG, Xiao X, Zenyuk IV. Operando X-ray tomography and sub-second radiography for characterizing transport in polymer electrolyte membrane electrolyzer. Electrochim Acta 2018;276:424–33.

[104] Feng Q, Yuan X-Z, Liu G, Wei B, Zhang Z, Li H, Wang H. A review of proton exchange membrane water electrolysis on degradation mechanisms and mitigation strategies. J Power Sources 2017;366:33–55.

[105] Chandesris M, Médeau V, Guillet N, Chelghoum S, Thoby D, Fouda-Onana F. Membrane degradation in PEM water electrolyzer: Numerical modeling and experimental evidence of the influence of temperature and current density. Int J Hydrogen Energy 2015;40(3):1353–66.

[106] Fouda-Onana F, Chandesris M, Médeau V, Chelghoum S, Thoby D, Guillet N. Investigation on the degradation of MEAs for PEM water electrolysers part I: Effects of testing conditions on MEA performances and membrane properties. Int J Hydrogen Energy 2016;41(38):16627–36.

[107] Siracusano S, Hodnik N, Jovanovic P, Ruiz-Zepeda F, Šala M, Baglio V, Aricò AS. New insights into the stability of a high performance nanostructured catalyst for sustainable water electrolysis. Nano Energy 2017;40:618–32.

[108] Weiß A, Siebel A, Bernt M, Shen T, Tileli V, Gasteiger H. Impact of intermittent operation on lifetime and performance of a PEM water electrolyzer. J Electrochem Soc 2019;166:F487–97.

[109] Papakonstantinou G, Algara-Siller G, Teschner D, Vidaković-Koch T, Schlögl R, Sundmacher K. Degradation study of a proton exchange membrane water electrolyzer under dynamic operation conditions. Appl Energy 2020;280:115911.

[110] Bernt M. Analysis of voltage losses and degradation phenomena in PEM water electrolyzers (Ph.D. dissertation), Technische Universität München; 2019, [Online]. Available: https://nbn-resolving.de/urn/resolver.pl?urn:nbn:de:bvb:91-diss-20190201-1463630-1-5.

[111] Frensch SH, Fouda-Onana F, Serre G, Thoby D, Araya SS, Kær SK. Influence of the operation mode on PEM water electrolysis degradation. Int J Hydrogen Energy 2019;44(57):29889–98.

[112] Akker J, Blok H, Budd C, Eggermont R, Guterman A, Lahaye D, Lansink Rotgerink J, Myerscough K, Prins C, Tromper T, Wadman W. A case study in the future challenges in electricity grid infrastructure. In: Study group mathematics with industry - SWI 2012. 2012, [Online]. Available: https://www.researchgate.net/publication/325951690_A_Case_Study_in_the_Future_Challenges_in_Electricity_Grid_Infrastructure.

[113] Parsons BK, Wan Y, Kirby B. Wind farm power fluctuations, ancillary services, and system operating impact analysis activities in the United States: Preprint. In: Conference: European wind energy conference, Copenhagen (DK), 02/07/2001–06/07/2001. National Renewable Energy Lab. (NREL), Golden, CO (United States); 2001, [Online]. Available: https://www.osti.gov/biblio/788752.

[114] Ceraolo M, Poli D. Fundamentals of electronic power conversion. In: Fundamentals of electric power engineering: From electromagnetics to power systems. IEEE; 2014, p. 239–90.

[115] Parache F, Schneider H, Turpin C, Richet N, Debellemanière O, Bru E, Thieu AT, Bertail C, Marot C. Impact of power converter current ripple on the degradation of PEM electrolyzer performances. Membranes 2022;12(2).

[116] Det Norske Veritas. Hydrogen forecast to 2050, energy transition outlook 2022. Tech. Rep., Det Norske Veritas; 2022, [Online]. Available: https://www.dnv.com/focus-areas/hydrogen/forecast-to-2050.html.

[117] International Energy Agency. The future of hydrogen. Tech. Rep., Paris: International Energy Agency; 2019, [Online]. Available: https://www.iea.org/reports/the-future-of-hydrogen.

[118] LAZARD. Lazard's levelized cost of hydrogen analysis. Tech. Rep., LAZARD; 2021, [Online]. Available: https://www.lazard.com/media/12qcxl1j/lazards-levelized-cost-of-hydrogen-analysis-vf.pdf.

[119] Esposito DV. Membraneless electrolyzers for low-cost hydrogen production in a renewable energy future. Joule 2017;1(4):651–8.

[120] European Comission. COMMISSION DELEGATED REGULATION (EU), supplementing Directive (EU) 2018/2001 of the European Parliament and of the Council by establishing a Union methodology setting out detailed rules for the production of renewable liquid and gaseous transport fuels of non-biological origin. Tech. Rep., European Comission; 2023, [Online]. Available: https://energy.ec.europa.eu/system/files/2023-02/C_2023_1087_1_EN_ACT_part1_v8.pdf.

[121] Moradpoor I, Syri S, Santasalo-Aarnio A. Green hydrogen production for oil refining – Finnish case. Renew Sustain Energy Rev 2023;175:113159.

[122] Ginsberg MJ, Venkatraman M, Esposito DV, Fthenakis VM. Minimizing the cost of hydrogen production through dynamic polymer electrolyte membrane electrolyzer operation. Cell Rep Phys Sci 2022;3(6):100935.

[123] California Energy Comission. 2021 Total system electric generation. 2023, Online, accessed 02-05-2023. [Online]. Available: https://www.energy.ca.gov/data-reports/energy-almanac/california-electricity-data/2021-total-system-electric-generation.

[124] Jang P, Beruvides M. Impact of the U.S. electric deregulation on california renewable investments. In: Proceedings of the 2020 IISE annual conference. 2020, [Online]. Available: https://www.researchgate.net/publication/353646914_Impact_of_the_US_Electric_Deregulation_on_California_Renewable_Investments.