



Exploring the state-of-operation of proton exchange membrane electrolyzers

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ABSTRACT

Proton exchange membrane electrolytic cells (PEMECs) have the potential to provide green Hydrogen as a sustainable energy source. PEMEC has already been applied at an industrially relevant scale. However, it still faces challenges regarding reliability and durability, especially in long-term operation. This review emphasizes the need for standardizing the cell configuration, the testing protocols, and the evaluation procedures to attain the optimum operation settings, and eventually precisely evaluating the degradation rate. Potential physico-chemical and electrical operational health indicators are described to identify the degradation of a distinct cell component in a running PEMEC. The reliable evaluation of degradation rate via operational health indicators with a robust supervisory system under stringent operating conditions is likely to diagnose the degradation mechanism. By developing incremental empirical degradation models via mapping a correlation between the history of proposed operational health indicators, the instantaneous degradation rate can be quantified. This approach, in turn, enables us to determine the state-of-operation of an electrolyzer during service, thereby benchmarking the durability of PEMEC. Finally, with the target of scaling up and fulfilling the commercial demands for PEMEC, the significance and literature contributions regarding operation management and prognostics are expressed.

1. Introduction

Hydrogen has emerged as a viable option for future energy transition scenarios owing to escalating energy demands, climate change concerns, and the need for efficient energy storage of a fluctuating renewable energy supply from wind or solar. It offers a wide range of applications in the energy sector and can be utilized in industrial processes, residential power supply, and mobility technology [1]. This is why, it is imperative to generate a substantial quantity of Hydrogen via cost-effective and ecologically sustainable production processes [2]. To promote the transition to a zero-carbon economy, the European Commission has developed a hydrogen strategy, and several European Union (EU) member states are engaged in its implementation [3–5].

One of the most promising technologies for this electrochemical energy conversion process are proton exchange membrane electrolytic cells (PEMECs) [6]. The findings of life-cycle assessment indicate that, while operating on renewable energy sources, PEMECs have the

potential to reduce CO₂ emissions by up to 75% as compared to conventional technologies [7]. PEMEC can operate at high current densities with more dynamic operation profiles than comparable technologies [8], which is maybe most important considering its potential use with a fluctuating energy source. The high current densities also allow for a more compact system design. However, improving the lifespan of PEMEC is still crucial due to the high capital expenditure (CAPEX) for PEMEC and electrolysis systems in general. Despite being one of the most prominent advantages of PEMEC, only 11% of publications deal with its dynamic operation and the impact on lifetime [9]. An expert elicitation study reported seven years of reliable operation for PEMEC and a 10-year continuous service life until 2030 [10]. However, there are still remaining challenges to fully realize the commercialization of PEMEC units.

The acceleration of PEMEC's commercialization is possible provided that the existing challenges, including failure diagnosis, identification of degradation type, degradation mitigation, performance regeneration,

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and long-term sustainability issues are resolved. Under any operation mode, PEMEC undergoes degradation either reversible or irreversible [11–13]. These degradation mechanisms do not occur standalone but rather interrelated and aggravate one another, posing significant challenges to the durable operation of PEMEC, particularly in the dynamic operation mode. The comprehensive analysis of accelerated stress tests reveals the complex degradation mechanisms, including catalyst deterioration and ionomer breakdown, which eventually lead to mechanical failures over time [14,15]. This indicates that degradation of PEMEC majorly affects the key component, such as the membrane electrode assembly, which is highly susceptible to chemical and mechanical stressors. Hence, it is of utmost importance to have a comprehensive understanding of the unit's behaviour in various operational modes at laboratory, pilot, and industrially relevant scales.

The precise determination of a performance indicator such as operational history of degradation rate is crucial to diagnose cell performance reduction over time. Various diagnostic tools are known and have been utilized for proton exchange membrane fuel cells (PEMFCs) [16]. In real-time monitoring of fuel cells and electrolyzers, degradation rate can be used as a diagnostic tool to estimate state-of-operation (SoO), referring to its existing status in terms of efficiency and durability. A comparable methodology has also been conferred in gas turbine engines applying four modules: data management, health, diagnostic, and lifetime [17]. Currently, reliable determination of the degradation rate for PEMEC remains challenging, which is why literature data are hard to compare, further hindering the accurate prediction of the lifespan of PEMECs. This underlines the need for standardized protocols to accurately assess degradation across different operational modes. Furthermore, the inconsistencies in testing protocols contribute to difficulties in comparing degradation data across laboratories, making it challenging to develop universally applicable lifetime prediction models [18]. This standardization could help in addressing variances in degradation rates, enabling a more reliable assessment of the SoO of PEMECs.

This article addresses promising tools for SoO diagnostics of a running PEMEC, which can aid in early detection of failure mode and degradation mechanism, thus avoiding irreversible degradation. Utilizing online monitoring can facilitate the implementation of appropriate maintenance measures, such as adjusting the load profile, and precisely predicting the remaining lifespan. The scaling up of PEMEC implementation and extending lifespan could potentially be achieved this way. The outline of this paper is as follows: first the multiple degradation processes involved in PEMEC are described, then the degradation rate under different operating modes is outlined and finally the online operational health monitoring of an operating PEMEC is derived.

2. Degradation mechanism

This section provides a brief overview of the literature on degradation mechanisms and reversible/irreversible losses in single PEMECs. It is essential to comprehend the degradation mechanisms of all the components of PEMEC. Fig. 1 depicts the components of a single PEMEC, including the two catalyst layers (CLs), facilitation the Oxygen evolution reaction (OER) and Hydrogen evolution reaction (HER), referred to as anode and cathode, respectively. Further components are proton exchange membrane (PEM), porous transport layers (PTLs), and bipolar plates (BPs). Another crucial component is the sealings, which are not included in Fig. 1.

The key component, the membrane electrode assembly (MEA), typically includes three layers (MEA-3); a membrane coated with platinum group metals (PGMs) on the anode and the cathode side, respectively. The MEA is alternatively referred to as the catalyst coated membrane (CCM). Various terminologies have been established for the individual component of PEMECs and PEMFCs. A few terms are interchangeable and might lead to confusion. The term MEA may also include the two PTL layers (referred as MEA-5) and the two additional sealings (MEA-7). In fuel cells, diffusion is the dominant effect for gas transport

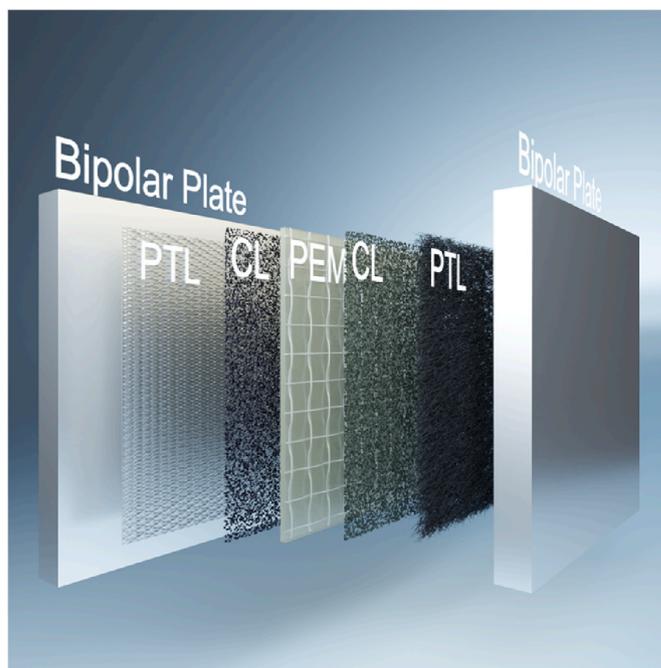


Fig. 1. Schematic diagram of the components of a single cell PEM electrolyzer.

[19]. This is why the PTL layers are called gas diffusion layers (GDLs). When the GDLs are coated with the catalyst rather than membrane, they are referred to as gas diffusion electrodes (GDEs). Since the subject of this review is PEMEC, we have chosen the term PTLs instead of GDLs. To correlate the degradation mechanism to the cell components, we refer to the MEA-3 configuration as MEA in the following.

PGMs are frequently utilized as catalysts in PEMEC because of the harsh electrochemical conditions, including elevated temperature, low pH, voltages above 1.5 V, and rich oxidant concentrations at the anode [20]. Catalyst degradation occurs in this environment by dissolution, aggregation, surface blockage by external metal cations, as well as support passivation and corrosion. These factors can lead to an increase in electrical contact resistance and a decrease in the catalyst's active surface area [21]. Currently, iridium-based materials are used as anode catalysts, albeit being rare and costly [22,23]. Several studies have proposed the OER mechanism and reported the formation of Ir-based intermediates and their switching from one oxidation state to another, as well as experimentally using XAS and XPS-based techniques [24–29]. The most relevant degradation effect is the electrochemical dissolution of iridium (Ir) at water splitting potential, the mechanism of which is not yet entirely understood [23]. Ir dissolution may lead to an overall cell voltage increase as less OER catalyst is available inside the catalyst layer. Fig. 2a shows the impact of low Ir loading (0.08 mg cm^{-2}) on cell performance and compares it to an industry standard of 3 mg cm^{-2} [30]. Over a runtime of 4500 h, the operating voltage of the cell with the low loading increased significantly, but the reference cell with high loading remained rather stable. According to authors, during electrolysis operation, Ir was dissolved and deposited inside the membrane as well as on the cathode side, leaving only 30% of initial Ir catalyst at the anode, thus leaving little headspace for losses. Fig. 2b illustrates the catalyst degradation mechanism, centred on Ir dissolution. Here, it is proposed that Ir dissolves into the membrane until it reaches the cathode side, where it forms Pt–Ir particles and mainly deposits on Pt particles. The Pt-dissolution, on the other hand, is comparably little. Fig. 2c shows the proposed pathways of Ir-dissolution. Initially, it is assumed that metallic Ir is oxidized to IrOx at a certain voltage. Subsequently, the water splitting reaction occurs under an applied potential, shown by the blue arrows. Afterwards, depending on whether the applied potential at the Ir-catalyst is higher or lower than $1.6 V_{\text{RHE}}$, different pathways for

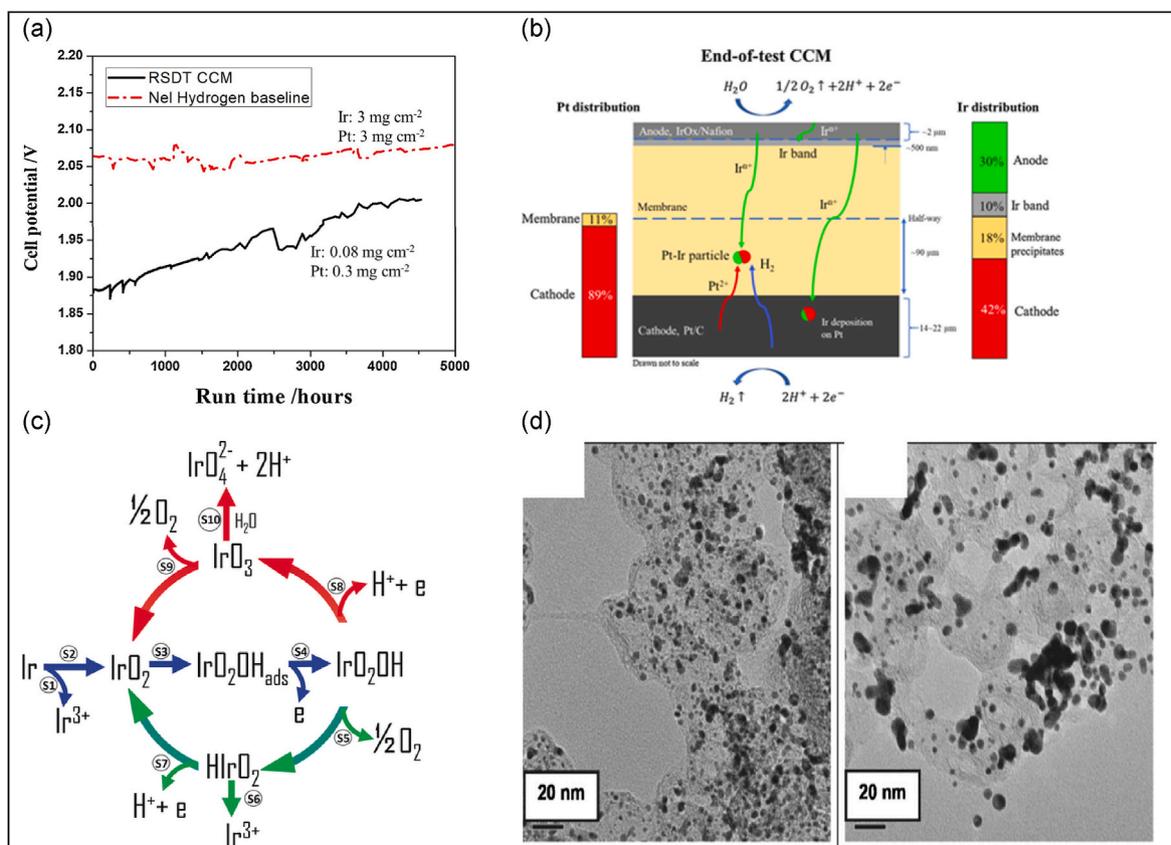


Fig. 2. (a) Comparison of cell voltage at high and low catalyst loading. Low catalyst loading results in low reserves for the Ir-dissolution effect on cell voltage. (b) Illustration of Pt–Ir precipitates and Ir band formation due to dissolution of Ir in a membrane. (a) and (b) adapted with permission [30]. Copyright 2020, Elsevier. (c) Proposed dissolution pathways for Ir under water electrolysis conditions. Blue arrows indicate intermediate steps independent of electrode material and applied potential. Green arrows show a pathway during OER at low potential, whereas red arrows indicate the pathway during OER at high potential. Adapted with permission [23]. Copyright 2018, John Wiley and Sons. (d) Carbon supported platinum catalyst particles before and after 529 h degradation run of PEMFC. Left shows the pristine catalyst particles, right agglomerated particles. Adapted with permission [33]. Copyright 2007, IOP Publishing. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

dissolution exist [23]. The red arrows indicate the pathway at high potential, where IrO₄²⁻ may be generated, whereas the green arrows denote the low potential pathway, where Ir³⁺ may be produced. According to a recent study, iridium loading should be lowered from 2 mg cm⁻² to 0.05 mg cm⁻² to facilitate its large-scale deployment, given iridium's high cost and restricted availability [20]. Novel material design strategies are required to sustain a high activity and electrochemical durability of the OER. Nano structuring of Ir, alloying Ir with hetero metals, and anchoring Ir on a supporting substrate have been utilized in this context [31]. Further research is needed to make these approaches feasible for practical implementation. RuO₂ was also used due to its lower overpotential for the OER. Its dissolution rate, however, is far more rapid, because volatile RuO₄ is produced [32]. Apart from the degradation of the anode catalyst, the widely used cathode catalyst platinum (Pt), is also affected by ageing effects. Fig. 2d shows the agglomeration of Pt suspended on carbon. Small Pt particles agglomerated to bigger particles, lowering the electrochemically active surface area [33]. Catalyst deactivation can also happen when the catalyst surface is covered with external metal cations (such as Na⁺, Ca²⁺, Cu²⁺, Ni²⁺, Fe³⁺) produced by the corrosion of cell and stack parts or impurities in the feed water [21,32].

The membrane is another critical component that is affected by chemical and mechanical degradation. Membrane degradation attributed to chemical or electrochemical reactions are typically initiated by radicals attacking the membrane backbone. These radicals are formed due to oxygen permeation through the membrane, which can produce H₂O₂ due to H₂ reaction with the permeated oxygen on the cathode

[33].

In the presence of metal cation impurities like Fe^{x+}, H₂O₂ can decompose into hydroxyl (HO●) and hydroperoxyl (HO₂●) radicals [34,35]. These oxidizing species can subsequently react with the ionomer, leading to the removal of functional groups [34], causing the membrane thinning over time. Information about membrane degradation can be obtained from the in-situ measurements of sulphur emission rate (SER) and fluoride release rate (FRR) in the effluent water [21,36]. A thinner membrane leads to an increase in oxygen crossover, thereby

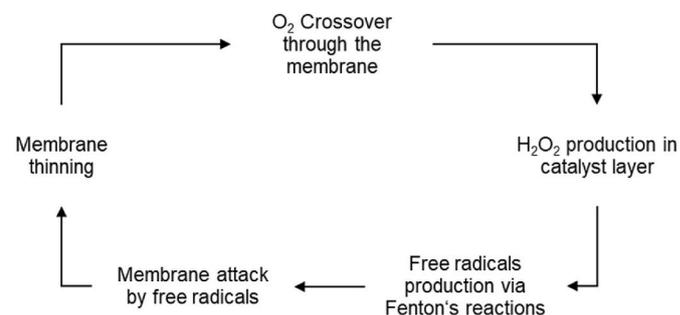


Fig. 3. The self-amplifying cycle of oxygen crossover through the membrane of PEMECs involves the following mechanism: Oxygen crossover serves as the primary source of radicals formation, which degrade the membrane. This degradation results in the thinning of the membrane, thereby increasing the rate of oxygen crossover, redrawn from reference [37].

self-amplifying this degradation effect. Fig. 3 shows the degradation cycle induced by oxygen crossover through the membrane. Furthermore, differences in membrane thickness pre- and post-electrolysis constitute valuable ex-situ evidence [21]. The external metal cations could also contribute to an increase in the ohmic losses across the membrane. The strong affinity of these ions to the membrane compared to protons enables them to migrate into the membrane, where they potentially occupy the ion exchange sites of the membrane. It was, however, previously shown that the poisoning of the catalyst and membrane can in some cases be reversed by treating the membrane with a solution of $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ [21,32]. The failures happening within the initial 1000 h of operation are typically triggered by mechanical degradation, involving punctures, cracks, mechanical stress, and pressure deviations. Membrane failure can occur after long-term operation, possibly leading to short-circuiting or gas crossover and thus the formation of potentially explosive Hydrogen and Oxygen mixtures [21,32].

The roughness of the PTL surface can also contribute to membrane degradation [21,34]. It was also reported that a non-uniform distribution of water can lead to an unequal distribution of current density (j), which may produce an inconsistent distribution of heat and, ultimately, hotspots on the membrane might appear [38]. Such potential causes of degradation could be avoided by applying uniform pressure during compression of the PEMEC. The excellent electrical conductivity and strong corrosion resistance of titanium-based felt, sintered powder, mesh, and foam render them suitable for use as the anode PTL. Contact resistance can increase due to titanium (Ti) passivation caused by the harsh anode environment. This passivation layer can dissipate as the membrane degrades and fluoride ions are released. This, in turn, starts the corrosion of PTL. Additionally, mass transfer losses can be caused by an irregular pore structure of PTL. On the cathode side, using Ti-based components can lead to them experiencing Hydrogen embrittlement after prolonged exposure. Though coating PTL and BPs with noble metals (Pt, Au, Ir) could potentially help to avoid degradation, it also increases the cost [31,32]. Niobium was proposed as a cost-effective substitute coating material, still it was found to be only appropriate for the anode side since the cracks formed in the niobium layer caused by Hydrogen embrittlement on the cathode side [39]. For the cathode PTL, carbon-based paper or non-woven fibers is predominantly utilized owing to its high electrical conductivity, corrosion resistance, and excellent compression properties [40,41].

The degradation of PEMEC reduces its performance over time. It is crucial, therefore, to understand reversible and irreversible losses to effectively mitigate them. Sudden adjustment of current or voltage to flush oxygen bubbles from the anode, catalyst regeneration due to change in oxidation state at low current density, gas expulsion stuck in the catalyst micropores by load variations, chemical removal of passivation layer on the PTLs and BPs, and acid removal of MEA contamination may improve performance because they are attributed to reversible losses [42–44]. However, dynamic mode, which includes load fluctuation, partial loading, on/off cycles, and input power quality, can incur extra losses that must be resolved. A recent review paper discussed the impact of dynamic mode and suggested optimizing PEMEC under dynamic mode using data-driven approaches [9]. On the other hand, irreversible losses include membrane thinning and catalyst degradation which may occur during both static and dynamic operation modes. As for corrosion of cell components, it corresponds to both reversible and irreversible divisions. In general, all degradation mechanisms discussed above are involved in reducing the lifetime of PEMEC.

3. Degradation rate

Degradation rate (DR) is defined as the rate at which the performance of a cell deteriorates over time, using a particular operational health indicator. State-of-the-art for assessing DR, is tracking the cell voltage over time [45]. The standard unit of measurement is $\mu\text{V/h}$. In this regard, a positive sign denotes a decrease in performance, whereas a

negative sign indicates an increase in performance. Degradation rate of PEMEC described in the literature varies significantly. This is due to a lack of standardization among the laboratories. So, a strategic approach is required to ensure comparability and reliability. Prior to performing any degradation testing, it is crucial to activate (or “condition”) the membrane. However, a systematic methodology for membrane activation or conditioning is unavailable in the literature. For instance, a study on approaches to benchmarking highlights that the initial conditioning procedure profoundly influences test results and should be considered to draw precise figures [18].

Operating conditions are another very important aspect that affect the performance of the membrane and catalyst. Various parameters—for example temperature, flowrate, pressure, and current density—need to be optimized to enhance PEMEC’s durability and performance. An experimental study was conducted to explore temperature effect on cell performance at 75°C , 80°C , and 85°C [46]. The rise in temperature led to more Hydrogen generation, a lower activation potential, and an increase in exchange current density. Another research work pointed out that membrane thickness decreased by 50% in 8700 h at 80°C and 38500 h at 60°C [34]. It indicates that higher temperatures degrade the membrane which could be monitored by tracking the FRR. Also, thinner membranes enhance the gas crossover, which could lead to the formation of explosive mixtures. The increase in operating temperature increases the gas crossover, which amplifies the membrane thinning effect. Increasing the temperature from 60°C to 80°C elevates the oxygen permeability of the Nafion™ membrane by $\sim 45\%$ [47]. Moreover, a fivefold increase in degradation rate of PEMEC has also been observed when the temperature stressor was applied; the temperature raised from 60°C to 100°C (see T \rightarrow U in Fig. 4 and Table 1) [48,49]. This occurred because ionomer decomposition surged by a factor of 10 [48]. A similar observation has reported the acceleration in degradation rate when PEMEC was operated at temperature above 80°C (see Q \rightarrow R in Fig. 4 and Table 1) [50]. So, tracking of H_2 concentration at the anode and the

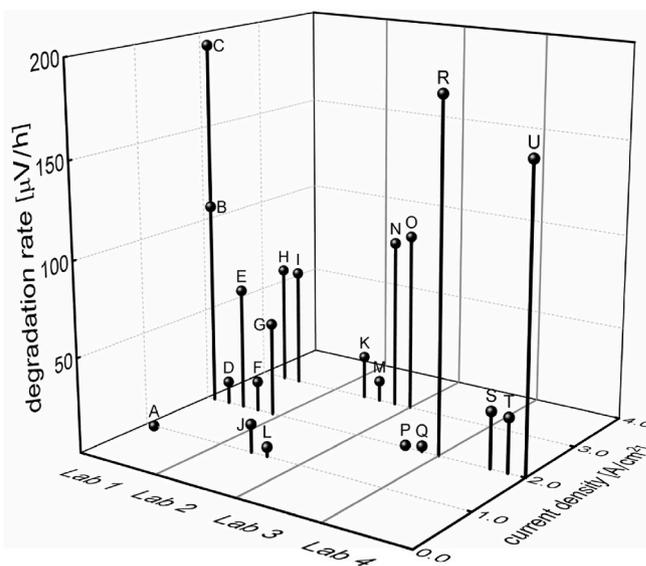


Fig. 4. Degradation rate influenced by current density and phenomena reported by four different comprehensive experimental studies. The data acquired is categorized into four groups based on Ti-passivation (Lab 1), anode catalyst loading (Lab 2), temperature increase (Lab 3), and high temperature stressor (Lab 4). A summary of data for each category is provided in Table 1. Labels scheme: A, B, C (Ti-PTL, 80°C , static mode); D (Pt coating on Ti-PTL, 80°C , static mode); E, F, G (Ti-PTL, 80°C , dynamic mode); H (Pt coating on Ti-PTL, 80°C , static mode); I (Pt coating on Ti-PTL, 80°C , dynamic mode); J, K (Ti-PTL, 80°C , static mode, lower anode loading); L, M (Ti-PTL, 80°C , static mode, higher anode loading); N (Ti-PTL, 80°C , dynamic mode, lower anode loading); O (Ti-PTL, 80°C , dynamic mode, lower anode loading); P, Q (Ti-PTL, 60°C and 80°C respectively, static mode); R (Ti-PTL, 90°C , static mode); S, T (Ti-PTL, 60°C , static mode); U (Ti-PTL, 100°C , static mode).

Table 1
Overview of degradation rate transition and its specified mechanism.

Lab	Temperature °C	Change in Configuration	Operation Mode	Average Degradation Rate $\mu\text{V}\cdot\text{h}^{-1}$	Rationales	References
1	80	A → B	Static	0 → 108	I	[54,59,69]
		B → C	Static	108 → 194	II	
		B → D	Static	108 → 12	III	
		C → E	Static → Dynamic	194 → 65	IV	
		E → F	Dynamic	65 → 16	V	
		F → G	Dynamic	16 → 50	VI	
		D → H	Static	12 → 63	VII	
		H → I	Static → Dynamic	63 → 63	VIII	
2	80	J → K	Static	15 → 23	IX	[44,55]
		L → M	Static	5 → 11		
		J → L	Static	15 → 5		
		K → M	Static	23 → 11		
		N → O	Static → Dynamic	90 → 95		
3	60 → 80 → 90	P → Q → R	Static	1.2 → 3 → 183.3	XI	[50]
4	60 → 60	S → T	Static	30 → 29	XII	[48,49]
	60 → 100	T → U	Static	29 → 158	XIII	

I: DR surged up from medium to high current density ($1 \rightarrow 2 \text{ A cm}^{-2}$) attributed to Ti-PTL passivation leading to a significant increase in ohmic losses.

II: DR increased gradually over time.

III: DR decreased significantly with Pt coating on Ti-PTL.

IV: DR reduced by periodic reductions in current attributed to reduction in ohmic losses.

V: DR depressed further by fewer and longer interruptions in current.

VI: DR increased again by more and shorter interruptions in current due to cathode degradation.

VII: DR increased from high to elevated current density ($2 \rightarrow 3 \text{ A cm}^{-2}$) due to the removal of the Pt coating from the Ti-PTL. This, in turn, led to higher ohmic and mass-transport losses.

VIII: DR did not exhibit changes at elevated current density (3 A cm^{-2}), changing from static to dynamic mode.

IX: DR increased as current density increased, and anode catalyst loading decreased, which was correlated with an increase in turnover frequency.

X: DR showed a minor increase in load cycling mode in contrast to steady-state mode. This is due to a decrease in series resistance attributed to membrane thinning in steady-state mode.

XI: DR accelerated above 80°C , attributed to increased membrane thinning and passivation of Ti-based cell components.

XII: DR reported in references [48,49] showed a slight difference.

XIII: DR increased fivefold when the cell was operated at 100°C rather than 60°C . This is attributed to 49% ohmic losses and 45% anode kinetic losses.

O_2 concentration at the cathode can be used as a vital diagnostic tool. All in all, this indicates that while PEMEC performance improves with elevated temperatures, it also promotes membrane degradation shortening its lifespan. Degradation of the membrane can potentially cause the PEM single cell or stack to fail or at least decrease the Hydrogen production efficiency.

A few studies have explored how changes in the volumetric flow rate of the water can affect the performance of PEMECs [46,51]. A water flow rate higher than the stoichiometric rate must be maintained to avoid membrane desiccation and to effectively remove heat from stacks and cells [52]. On the contrary, the inadequately low water stoichiometric ratio leads to a non-homogeneous distribution of hydration (catalyst and membrane), ultimately resulting in dehydration and a subsequent decrease in performance. This impact is significant at the cell exit and has been experimentally demonstrated as an increase in ohmic and mass transfer losses [53]. Thus, it is essential to optimize the flow rate according to the cell's characteristics, such as the pore size of PTL and the design of the flow channel, as well as the applied current density.

Current density is also a vital parameter that influences the performance of PEMEC. Static operation mode (constant current density) and dynamic operation mode (fluctuating current density) have been extensively studied in literature. Findings from one study indicate that by operating the PEMEC in static mode, the increase in current density ($1 \rightarrow 2$) $\text{A}\cdot\text{cm}^{-2}$ caused a 78% increase in ohmic resistance and occurred due to the passivation of Ti-based PTL. A significant decrease in degradation rate was observed when Pt coating was used on Ti-based PTL. Moreover, a 5 min current interruption led to a 61% recovery in cell voltage [54]. This impact is usually attributed to the removal of mass transfer losses [55,56], and irreversible losses are attributed to the passivation of Ti-based components [54,57–59]. Additionally, the

degradation rate increases due to changes in oxidation state [58] and dissolution of Ir above 1 A cm^{-2} [55], whereas current density below 1 A cm^{-2} results in high gas crossover in comparison to gas production rate [60,61], adversely influencing membrane life, as mentioned above. On the other hand, operations with fluctuating current density reduce reversible losses but introduce its own degradation effects [59]. Frequent shutoffs lead to Pt agglomeration at the cathode catalyst and an increase in membrane thinning [50]. Sudden changes in current density can lead to catalyst detachment by quickly forming bubbles [62]. Apart from that, at high current densities, gas accumulation can occur because the gas bubbles cannot escape from the PTL fast enough [63,64]. If the level of gas accumulation is high, the gas forms a barrier in the PTL, which prevents the water from reaching the catalyst layer [65,66]. In harsh cases, these gas accumulations can lead to inhomogeneous water distribution, even water starvation, resulting in inhomogeneous current distribution and hotspots [66–68]. This not only causes a decrease in efficiency, which can be observed by an increase in the monitored voltage, but also a reduction in durability. However, if the PEMEC is switched off as soon as the voltage increases, the reversible losses can be removed. By switching off the current, the evolution reactions come to a stop and no further gas is produced. The PEMEC is now filled with water again and the previously accumulated gas bubbles are removed from the water and transported away, except for a few trapped bubbles.

Fig. 4 illustrates the correlation between average degradation rate and current density. The data were collected from eight in-depth experimental studies done in four separate labs. Lab 1 investigated how the degradation rate was affected with and without coating of PTL in static and dynamic modes. Lab 2 examined the impact of anode catalyst loading under both static and dynamic operating modes. Lab 3

studied the decrease in durability caused by an increase in temperature, whereas Lab 4 similarly identified high temperature as a stressor that enhances degradation effects. Still, the data obtained from these laboratories cannot be directly compared because of differences in their testing procedure, cell components, and probably also differences in hardware used. The thirteen results from these studies are shown in Table 1.

To lower the cost of Hydrogen production, pressurized operation has also been recommended in some studies and summarized in a recent review paper [31]. In this case, to prevent explosions, the pressure needs to be defined in accordance with the characteristics of the membrane and its inherent gas crossover behaviour. It is reported in literature that the stack should operate with a Hydrogen pressure of 0.068 bar higher than the water pressure to reliably detect dangerous Hydrogen concentrations on the anode side in case of membrane failure [52].

To advance PEMEC technology and ensure its widespread adoption, it is vital to implement the standardization concept. Therefore, cell components, cell sizing and configuration, material characterization methods, testing procedures and protocols, etc. should be harmonized. A recent review states that the broad spectrum of degradation testing procedures renders it impractical for real-world implementation due to the limitation in comparing results [70]. Apart from that, by establishing a uniform method to quantify degradation rate, one can reliably perform the comparative assessment of PEMEC durability. In this regard, the EU has developed and implemented standards and released specific harmonized protocols for the characterization of PEMEC, at least at the European level [41,71–73]. Recently, Siemens Energy has also reported a strong need of standardization from PEMEC manufacturing up to module assembly [74]. However, implementation of standardization protocols encounters certain challenges. These include internal and external challenges which can hinder the ramping up of PEMEC [74]. The external factors include iridium shortage, which requires stack design with reduced iridium content, and iridium recycling. Also, a solid eco-system for PEMEC manufacturers, suppliers and sub-suppliers is required to fulfill the synergy of materials demand. The internal factors need the continuous optimization of stack whenever a new design is implemented. Therefore, standardization is crucial to develop a universal protocol for reliable evaluation of degradation rate. Nevertheless, its implementation has its own set of practical limitations.

The degradation in PEMECs is highly complex as on one hand it depends crucially on the design of the electrolyzers, their specific components and the operating conditions, and on the other hand the investigations of the degradation may target different objectives. To benchmark degradation of complex machines or systems, while maintaining a fair comparison of their lifetimes, standardized operating protocols, that clearly distinguish between static and dynamic load conditions, are advisable. However, if the degradation behaviour of specific components is the main objective of the investigation, a modification of the standard protocols may be useful, to focus on the degradation to respective components. In case the investigation of degradation points to the development of specific type of electrolyzer, the operating protocols of degradation experiments may have to take the specific characteristics of design, components and intended operation mode into account.

4. State-of-operation of a running PEM electrolyzer

Contrary to PEM fuel cells, the literature on PEMEC control, optimization and modelling is scarce [75]. The adaption of concepts from PEMFC to PEMEC can be feasible due to structural and process similarities of both systems [76]. However, the key differences between both systems such as function and operational principles, necessitate an in-depth investigation of SoO for PEMEC. In the following, two approaches are described to estimate the SoO of a running electrolyzer.

4.1. Online monitoring approach

Health monitoring and prognosis (PHM) is a key for ensuring the reliable and durable operation of PEMEC. Comparing the system's characteristics after different operation times allows to ascertain SoO, and the data collected from sensors can estimate remaining useful life (RUL) by adapting the concept from PEMFC [77–79]. This may provide insights into the degradation state, thereby assisting in the prevention of system breakdown [80]. Fuel cell researchers have made considerable advances in PHM over the past ten years due to its widespread application in engineering processes [81]. But no optimal method has yet been devised, therefore reliable RUL estimation is still a subject of ongoing research [82].

PEMEC degradation has been extensively studied by in-situ electrical testing methods, including polarization curve (IV), electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and current distribution mapping [83–87]. Comparing IV and EIS can differentiate between multiple causes of degradation. Cyclic voltammetry is useful for estimating the accessible electrochemical surface area, but its application is restricted to laboratory scale, requiring specific adjusted testing setups. Examples for ex-situ examination include scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to examine topological changes, and X-ray diffraction (XRD) to evaluate variations in the crystal size of the catalyst. These diagnostic tools can help with assessing the degradation mechanism in a PEMEC that exhibits an increase in degradation rate, but they are only compatible with off-line use. However, the real-time settings necessitate the need for online monitoring to detect faults at an early stage. In this regard, performance or operational health indicators and different approaches to PHM are discussed below.

The indicators which can be used to assess the operational health of a running electrolyzer are divided into two primary groups: physico-chemical and electrical health indicators, as shown in Fig. 5. Cell voltage is the typically used operational health indicator due to relative simplicity, rapidity, low cost, and ability to reduce computational complexity for modelling approaches. It, however, can only provide limited information on SoO of PEMEC. For example, gold ribbon electrodes were used to separate the total cell voltage into voltage drops at specific components: anode BPs and PTL, cathode BPs and GDL, and MEA [88]. The interfacial resistance accounted for 2–18% of the total ohmic losses, with the MEA resistance as the primary contributor, showing that the cell voltage can be influenced by a wide variety of mechanisms and resistances. In a recent study, a platinum-based dynamic Hydrogen electrode was deployed as a micro-reference electrode, which was in contact with membrane outside the active area, inside an isolated compartment of humidified Hydrogen [89]. Via this configuration, protonic membrane potential was assessed, and kinetic parameters of anode and cathode were examined individually. A second frequently used health indicator is the polarization curve [41], but it might impact electrolyzers running in static mode by inducing degradation due to the interruption needed to record the polarization curve. An electrolyzer operating in static mode undergoes degradation, influenced by fewer-prolonged interruptions or more frequent-shorter interruptions [59].

To acquire insight of the processes occurring inside the cell, it is necessary to also probe the cell resistance. For this, EIS is an extremely powerful tool for analyzing and isolating multiple processes that take place at different frequencies. This is due to different relaxation times for each different process [90]. The non-destructive aspects of EIS have made its extensive implementation in PEMFC development [91]. Causality, linearity, stationarity, and stability are the four requirements that the system must follow for the reliable EIS study [92,93]. If the impedance spectrum satisfies these four characteristics, the real and imaginary parts or the phase angle and modulus of the complex impedance are interdependent and can be computed from each other using the Kramers-Kronig (KK) relation [94]. The measured real part of

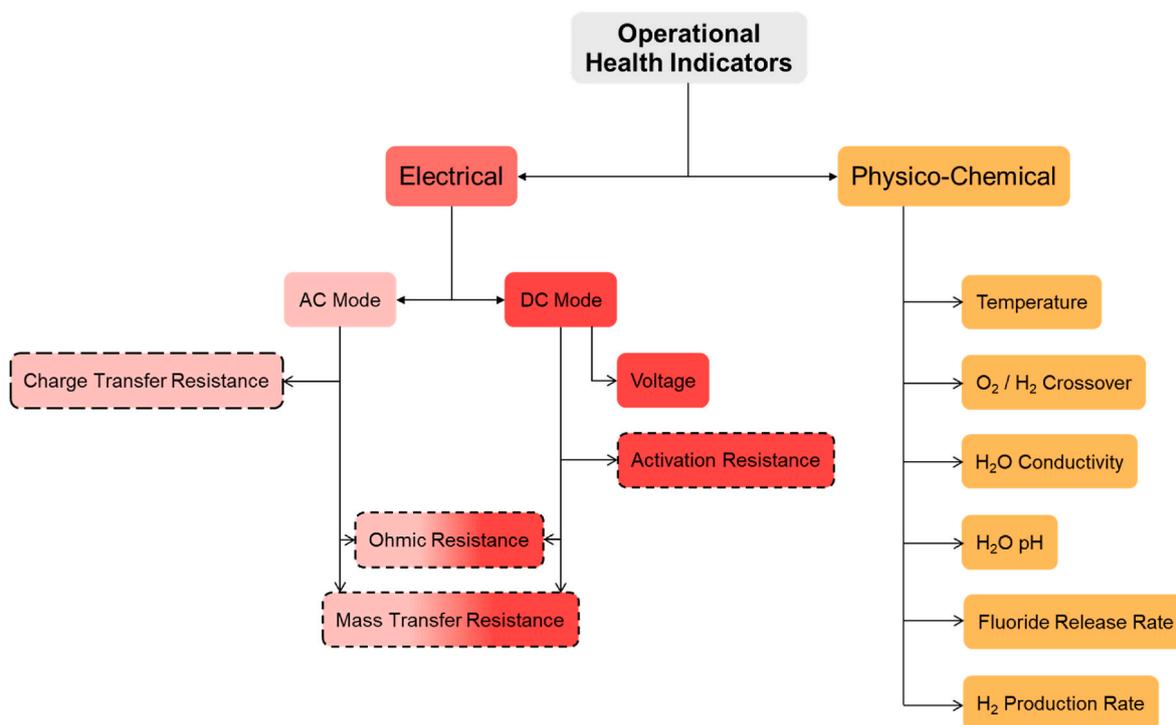


Fig. 5. Summary of operational health indicators for a PEMEC in operation. Boxes outlined with dashed lines represent the parameters, that can be calculated in offline mode.

the impedance can be utilized as input to calculate the imaginary part, and the reverse is also valid (real-to-imaginary or imaginary-to-real). The presence of artifacts in impedance spectra can be identified by comparing the computed and measured imaginary parts; differ from each other. The effectiveness of KK relation is hindered by its requirement to use specific values of impedance at the frequency extremes—zero to infinity—during the transformation, which are beyond the measurable limit. Consequently, KK relation was revised, and Zweipol-Hilbert Transform (Z-HIT) was introduced [95]. KK relation can be used as an easy and quick method to determine whether the measured data is free of experimental errors. Moreover, it extrapolates the spectra to frequency extremes mentioned above. On the other hand, Z-HIT is only applied on the measured data and can be used to identify the artifacts appear [96] at low or high frequencies. Linearity can be achieved by applying a very low perturbing signal, however, achieving stationarity is not possible in real-life scenarios. For instance, PEMEC exhibits non-stationary behaviour due to unstable cell voltage when operated under galvanostatic conditions. Artifact, such as drifts, may be readily visible at very low frequencies, such as millihertz (mHz) or microhertz (μ Hz). Another artifact, such as induction effects, is usually apparent at high frequencies. These artifacts can be eliminated by reconstructing the impedance spectra by Z-HIT approximation using artifact free frequency range (typically 1 Hz-1KHz).

According to EU harmonized protocol, EIS should be performed within the frequency range of 0.01 Hz and 1 MHz, depending upon the system's characteristics [71]. However, our PEMEC-related experience reveals that a frequency range of 100 mHz to \sim 20 KHz is enough for conducting adequate investigation. Nevertheless, the selection of suitable range of frequency depends on the specific cell [15] and electrical cables. EIS measurements are often performed under galvanostatic mode for PEMEC, but for potentiostatic mode, the applied AC potential must be greater than thermoneutral voltage [41]. The impedance spectra can be analyzed using equivalent circuit modelling, which involves the data fitting to determine the specific values of resistances and capacitances that represent the response mechanisms [97]. However, a fundamental understanding of the system is necessary to develop a suitable circuit

model. If the system is unknown or complex, Distribution of Relaxation Times (DRT) can be used as a complementary analytical tool [98]. The internal electrochemical processes can be reliably and quantitatively understood using this technique. The results are usually shown as peaks, where each peak indicates a process or two processes having the same relaxation time. A good circuit model can be developed in support of these peaks.

The rate-determining step and the effects of various phenomena on the performance and durability of electrolysis has been investigated using EIS [11]. In addition, a straightforward mathematical model that relies on both the polarization curve and impedance was presented in references. [54,58] This approach links charge transfer resistance to exchange current density, ohmic losses to ohmic resistance, and mass transfer losses to an additional semicircle at a very low frequency impedance. Therefore, EIS is an excellent non-invasive diagnostic tool for determining the SoO of PEMEC via online monitoring. However, its analysis must be conducted offline to determine if a system shutdown is essential.

Another operational health indicator that is related to power consumption is to measure the Hydrogen generation rate. Very little literature is available on this subject. The optimal cell parameters and a correlation between Hydrogen generation and power consumption can be examined using soap flow meters [99], H₂ flow meters [51], and thermal mass flow meters [100]. Also, online monitoring requires water quality sampling, featuring characteristics such as pH and conductivity. Water conductivity is affected by catalyst erosion, membrane thinning, and corrosion of cell or stack components. So, continuous monitoring of water conductivity by a probe can help diagnose degradation. In addition, nonstop recording of gas crossover using either gas chromatograph [101,102] or electrochemical cell analyzer [60], as well as FRR via ion chromatography, are equally essential. It was also reported that online monitoring of FRR using ion chromatography during water electrolysis can be conducted [36]. The PEMEC operation can be further maintained within the optimal temperature range by installing temperature sensors within the cell and water tank. The installation of flow meters between pump and cell ensures the amount of water entering the cell, which can

avoid the possible damages caused by irregular flow rate of water. Outside of the cell/stack itself, ultrasonic sensors are required to measure the water level in the reservoir to avoid an insufficient supply of water for the PEMEC. Figs. 5 and 6 show a summary of possible health indicators and their corresponding positions on the test stand, respectively.

The integration of the above-mentioned health indicators has not been fully realized in any experimental work, yet some studies have partially implemented it to provide the insights into the DR of the cell components [14,48–50]. In a recent work, the authors deployed gas chromatograph and conductivity probe in parallel to measure cell voltage to track the impact of elevated temperature on the DR [48]. FRR was also measured to monitor the degradation of membrane, although in the offline mode. Fig. 7a–c depict the cell voltage, H₂ contents into O₂ compartment and FRR in the discarded cathode drag water, and conductivity for a duration of 300 h, respectively.

The results indicate that PEMEC operation at elevated temperature (100 °C) enhanced the performance (lower cell voltage; Fig. 7a) while concurrently accelerated the H₂ gas crossover and FRR (Fig. 7b) and increased the water conductivity for the anode loop (Fig. 7c). The authors mentioned that elevated temperature is a stress factor that caused 5 times higher degradation rate in comparison to state-of-the-art temperature (60 °C) due to 49% ohmic loss and 45% anode kinetic loss. In another study, an evident correlation between FRR in the effluent anode water and H₂ crossover water was observed (Fig. 7d). When PEMEC was subjected to accelerated stress test at 80 °C, ~13% increase in H₂ contents into O₂ compartment, 8.5% increase in cumulative FRR and 1.6-fold higher increase in high-frequency resistance were noticed [14]. The authors highlighted that online monitoring of H₂ crossover is a significant health indicator that is associated with chemical degradation of membrane. Correspondingly, FRR being closely related to the membrane degradation, is a vital health indicator and its online monitoring may show transients in FRR production. In a contemporary investigation, automated ion chromatography can conduct continuous monitoring of FRR effectively [36]. Fig. 7e shows a linear relation of FRR and conductivity of cathode water loop. Moreover, the authors indicated that current density and temperature are crucial parameters influencing the FRR, irrespective of membrane thickness. Although the FRR at the cathode side causes irreversible membrane degradation due to oxygen permeation during operation, little literature has focused on

investigating O₂ levels in H₂ [60]. Therefore, the real-time FRR and oxygen crossover monitoring can assist in implementing effective interventions that can prevent the PEMEC from permanent damage.

4.2. Model- and data-based approach

For PEMEC, fundamental research on state-of-the-art diagnostic approaches based on dynamic modelling [103], balance-of-plant modelling [104–106], and signal or data processing [107,108] has been conducted. However, further comprehensive development of these approaches is still required. Model-based, data-driven, and hybrid methods were used to estimate PEMFC lifetime [40]. Model-based approaches are more intuitive since they apply physical laws to model system operation. Thus, the degradation progression of individual system components, whether alone or in interaction with other components, can be proposed. However, a false prediction may arise due to missing of an unidentified degradation phenomenon. This is why, it is crucial to combine approaches that are driven by models and data. Data-driven approaches are applied for complicated systems in which modelling the degradation process is challenging. This method relies on a history of degradation to foresee future performance without identifying individual degradation processes. Complex non-linear relations are established during the training phase, and the end of life is predicted during the prediction phase. A review on modelling guidelines for beginners provides a comprehensive compilation of the models for PEMEC available in the literature [109]. The equations were underlined for determining the open-circuit voltage, activation losses, ohmic losses, and mass transport losses. The models were categorized according to dynamic behaviour, thermal effects, and impact of two-phase flow. Additionally, empirical, and semi-empirical models were presented. It was determined that the lack of certain models' validation with experimental data, limited range of proposed models for dynamic behaviour, and absence of two-phase flow dynamics hinder the appropriate assessment of PEMEC performance. Besides, the models should incorporate the effects of components aging, which has not yet been realized.

During the operation of PEMEC, several parameters influence the performance. Few studies have defined a specific measure and reported the impact on the operation of PEMEC [110,111], which is insufficient to assess the performance in a realistic electrolysis environment. In fuel cells, the uncertainty quantification and sensitivity analysis techniques

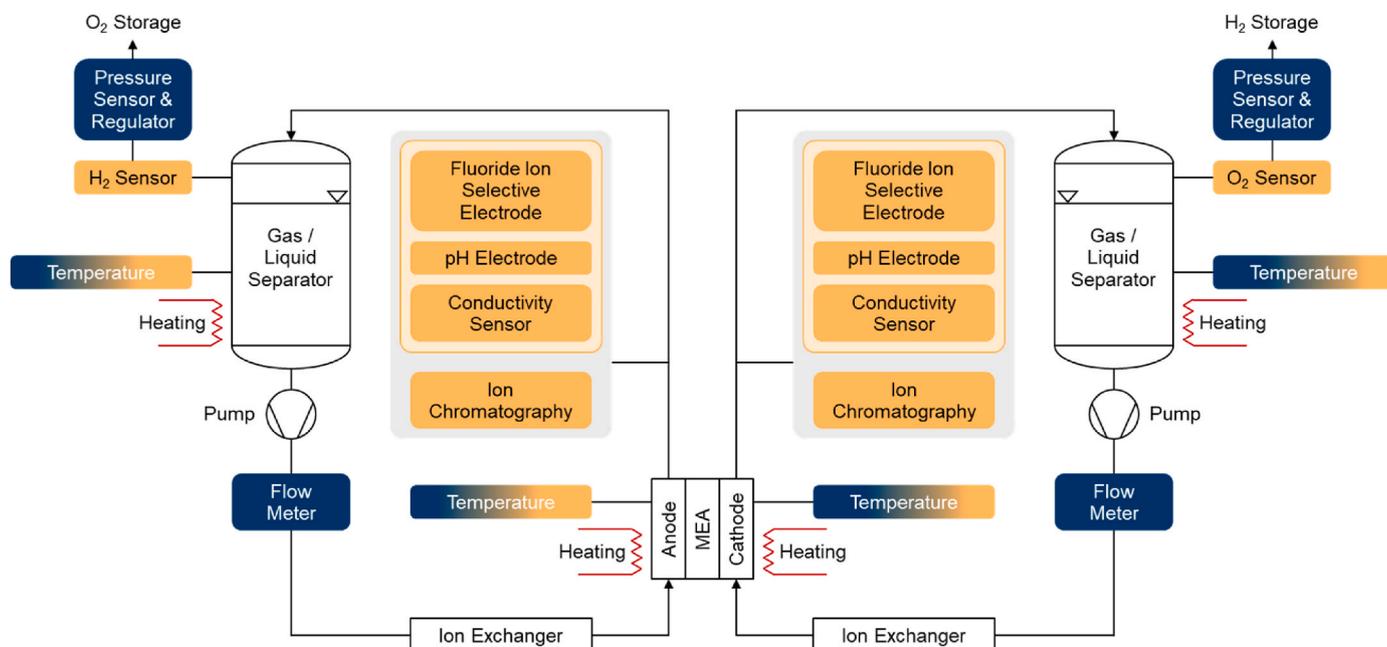


Fig. 6. Scheme of single cell test stand of PEMEC along with potential positions of sensors.

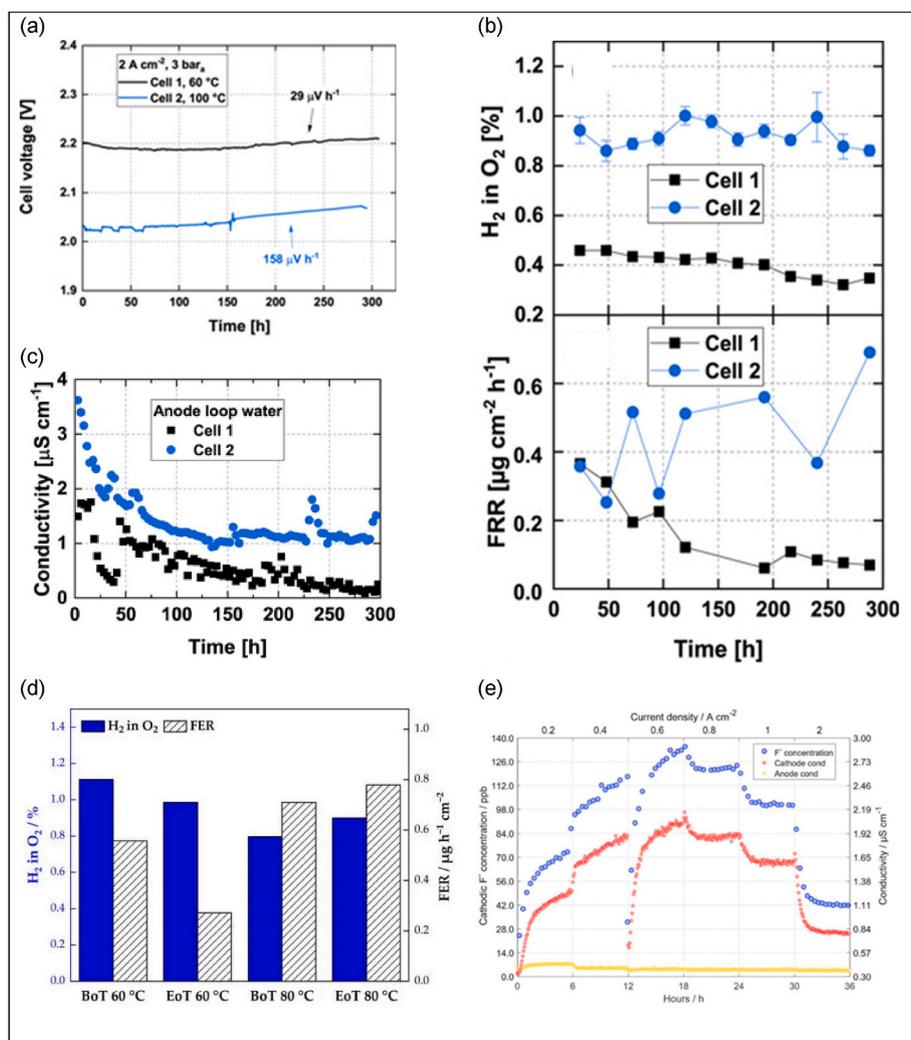


Fig. 7. Determination of degradation effects with the operation time under steady-state operation of PEMEC (a) cell voltage change, (b) H₂ content in O₂ on the anode side and FRR in the discarded cathode water (offline), (c) conductivity of anode water loop. (a), (b) and (c) adapted under the terms of the CC BY-NC-ND license [48]. Copyright 2021, IOP Science. (d) Change in FRR (offline) and H₂ crossover due to accelerated stress test at different temperatures. Adapted under the terms of the CC BY license [14]. Copyright 2023, MDPI Membranes. (e) Change in FRR (online) and water conductivity at the cathode side. Adapted with permission [36]. Copyright 2021, Elsevier.

have widely been implemented to improve the efficiency and lifespan [112–117]. Recently, a mathematical tool global sensitivity analysis (GSA) has also been employed in PEMEC to identify the influential and non-influential operating parameters and materials. The authors have first developed and validated a non-linear steady state model and accurately quantified the three objectives: hydrogen production rate, voltage efficiency and specific energy consumption [118]. By implementing GSA tool as an indicator on the model, the higher sensitivity indices in Fig. 8a represent that cross-section area of each cell, number of cells and current density greatly influence the hydrogen production rate. For voltage efficiency, the significant input parameter is current density, whereas insignificant parameters are cross-section area and membrane thickness. For energy consumption, the essential factors are GDL thickness and current density, whereas non-essential factors are thickness of membrane and cross-section area. Furthermore, generic algorithmic approach was integrated with GSA to achieve the maximum hydrogen production rate and concurrently reducing the specific energy consumption. Similarly, sensitivity analysis performed on a steady state physics-based PEMEC model showed that the membrane thickness, electronic conductivity and thickness of anode catalyst layer were the most prominent parameters influencing cell voltage [119]. However, further precise optimization strategies are still needed to explore and

validate in the real-world settings.

An energetic modelling approach, like the Bond Graph (BG) method, has been developed for such a complicated nonlinear dynamical system [104,106]. This multidisciplinary graphical tool applies the cause-and-effect principle to figure out the different energy flows in the system. Models at the global, subsystem, and component levels have developed using this approach. The measurement data was used to generate residuals to detect and isolate the faults. In a healthy system, the residuals are close to zero, and their deviation from zero indicates that a fault has happened [103]. Using the BG formalism, a dynamic model was developed and validated it on a 25 kW semi-industrial PEM electrolyzer [106]. Likewise, a robust and scalable BG model was established and tested offline by inserting errors [105]. The model was also applied online to a lab-scale commercial system supplied by Heliocentris®. As the membrane could not be removed, the diagnostic was conducted only by emulating the fault blockage (H₂ flow disrupted from electrolyzer to the storage bottle). The impact of this externally induced fault can be observed by the change in residual (purple line) in Fig. 8b. The residual was generated by incorporating the real-time data into BG model. When the valve was closed to disrupt the H₂ flow, the residual started approaching the lower threshold limit and crossed it at 50s. Upon opening the valve at 65s, the residual started moving towards lower

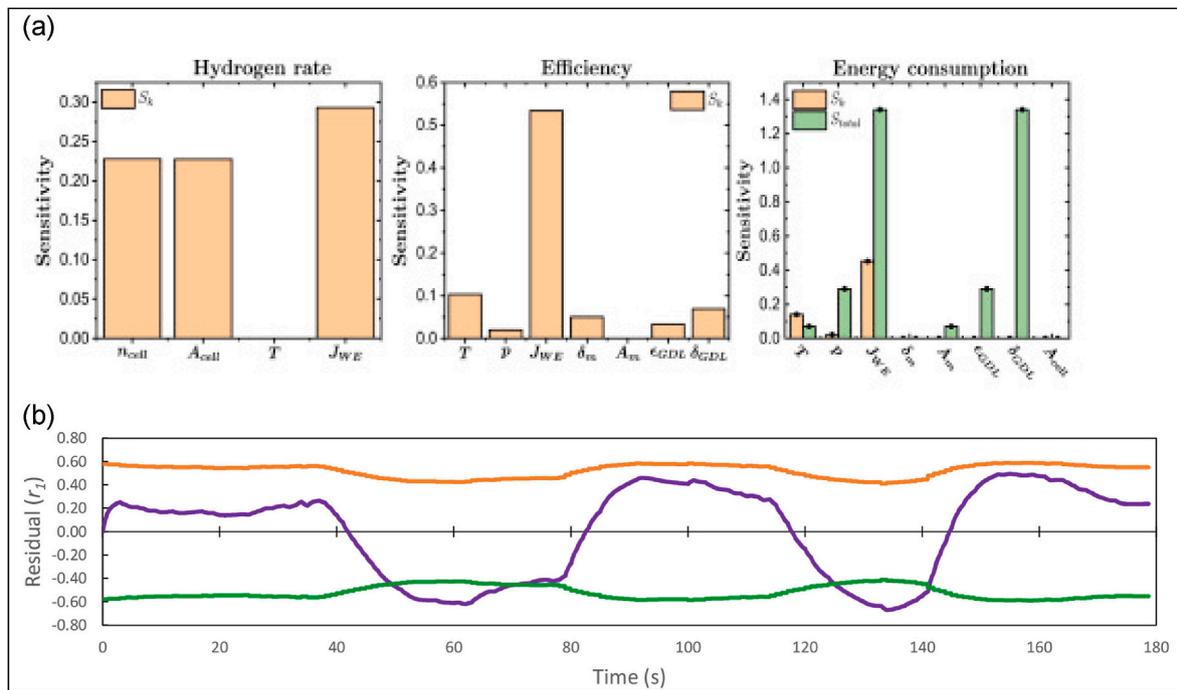


Fig. 8. (a) Sensitivity index of operating parameters and materials characteristics for hydrogen production rate, voltage efficiency, and energy consumption. Adapted with permission [118]. Copyright 2024, Elsevier. (b) Online detection of the impact of blockage fault on the performance of commercially available single cell PEM electrolyzer of 300 W connected to a hybrid multi-source platform. Adapted with permission [105]. Copyright 2022, Elsevier.

limit, and eventually entered within the limit at 70s. The reintroduction and removal of the fault can also be noticed at 120s and 135s, respectively. The consequence of the induced fault on the performance of PEM electrolyzer demonstrates the coupling of several subsystems. The information of good input and output of each subsystem can potentially identify the affected subsystem. Currently, there is no comprehensive model existing for large integrated PEMEC with balance of plant (BOP) to diagnose failure under dynamic intermittent operations [120]. Therefore, using a modular design approach to develop sub-models for individual failure mechanisms and incorporating them into the global model that can predict all failures is crucial.

The constraints encountered in physical modelling studies demand more research to precisely replicate real-world settings. For instance, multi-physics modeling is not only time-consuming but also necessitates the use of expensive computing resources. Recently, a data-driven approach was reported by combing the multi-physics modeling and system identification to speed-up the performance analysis of nonlinear dynamic behaviour of PEMEC [121,122]. However, this approach is only limited to single-input single-output system. Therefore, thorough investigations are required to apply it to multiple-inputs and multiple-outputs system in the first place. This might enable to develop a data-driven digital-twin model to accurately emulate the operation of lab-scale or industrial-scale PEMEC.

In this scenario, long-term experimental study under actual conditions and data processing seems essential. However, this requires an optimum BoP design that includes power supply, water management, Hydrogen generation, cooling, control subsystems, etc. To ensure reliable operation, each subsystem should be equipped with its own control program. BoP was designed, implemented, and validated in multiple operating settings for a medium-sized PEMEC by Mancera et al. [52] Thus, an effective supervisory system is sorely needed for continual monitoring and surveillance to determine the operational health status and potential risks [103]. Such a system needs data acquisition, data logging, and visualization tools. A novel framework, such as an industrial internet of things, was suggested in which commercial controllers sensed the system variables such as water level, temperature, voltage,

current, and H₂ flow rate [109]. Each entry was subsequently entered into a database using a communication network, and online access to it was obtained via an interactive program. The system demonstrated its feasibility when implemented on the PEMEC stack. Lately, a scalable and economical multichannel monitoring system has presented and deployed on a 1.2 kW PEMEC stack [123]. The parameters were successfully monitored in every individual cell inside the stack. Just recently, to simulate the dynamic characteristics of PEMEC stack's operation, mathematical models of stack and BOP were developed and validated with experimental data with ~10% error [124]. The authors have utilized hardware-in-loop simulation (HILS) technology to link all the devices with the mathematical models of the complete system. Fig. 9a shows the transient responses of stack voltage and input/output temperature. The authors described that the HILS responses attained steady state faster than the experimental data, attributed to unaccounted immeasurable heat losses.

Machine-learning (ML) based approaches are emerging as powerful tools to resolve the existing challenges associated with the aging of PEMEC [125]. The ML algorithms are trained and tested using experimental design data to attain the optimal performance of PEMEC [126]. These approaches allow predictive models to examine the impact of various factors including torque, temperature, current density, anode catalyst loading, and the role of pore diameter in the transport layer (PTL), which influence the degradation rate differently across the systems [127]. Via these predictive models, optimal design of PEMEC and hydrogen production rate can be estimated [128,129]. By tracking the performance indicators over time, such as voltage, predictive models can help to forecast the Remaining Useful Life (RUL) of PEMEC more reliably [130]. This predictive capability is crucial for industrial-scale PEMEC to optimize the operating conditions and prevent irreversible losses. At industrial scale, electrolyzers operate under transient load conditions, rendering it challenging to attain comparable and reproducible degradation rate. In a recent publication, a data-driven model was described that defines the correlation between voltage and operational conditions [108]. The model was developed by analyzing the generated data from a 0.5 MW industrial electrolyzer, operated for two

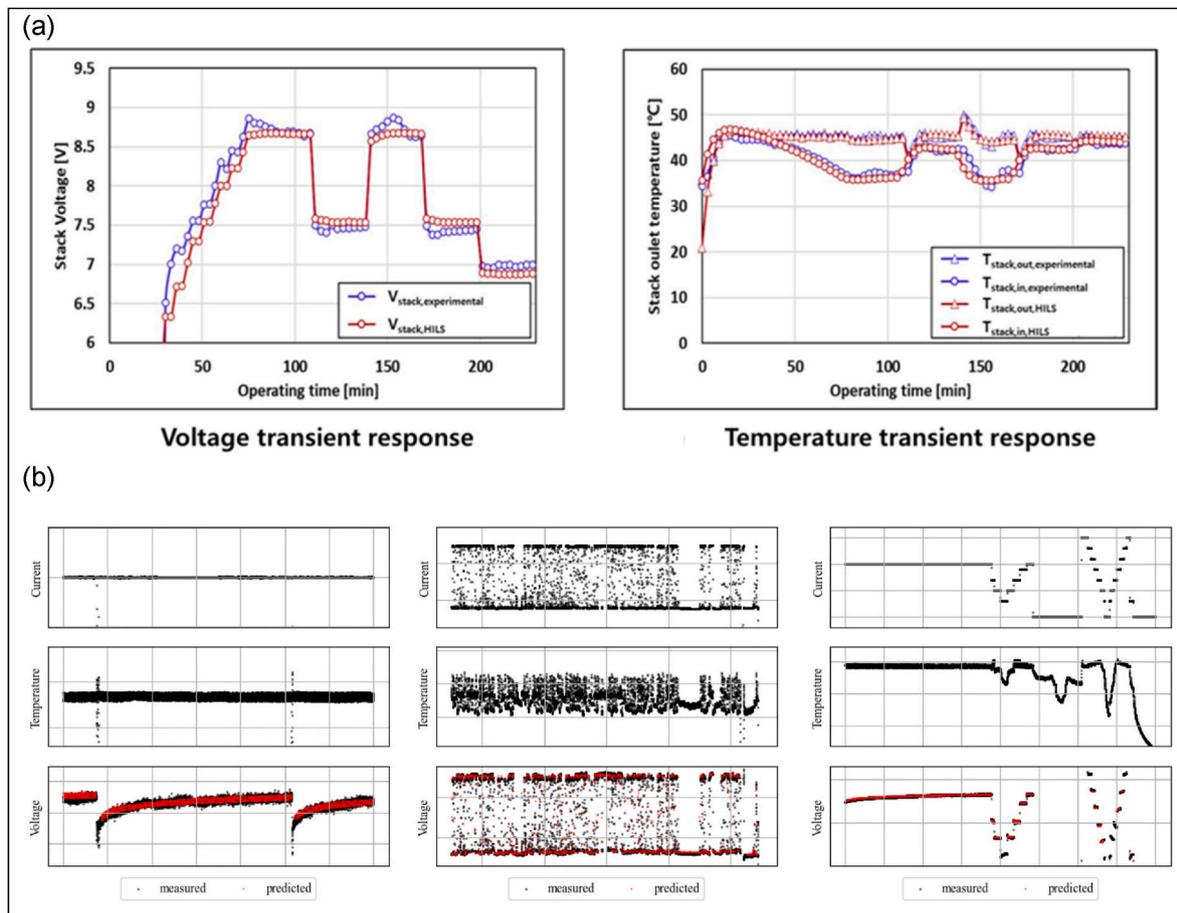


Fig. 9. (a) Transient responses dynamics of voltage and temperature using the hardware-in-loop simulation system and the experimental data produced using a PEM electrolyzer stack (300 W) manufactured by Horizon Fuel Cell. Adapted under the terms of the CC BY license [124]. Copyright 2023, MDPI Energies. (b) Data on voltage, temperature, and current for an industrial PEM electrolyzer operated under (left) constant operation with several starts, (middle) volatile operation, and (right) a combination of constant and volatile operation, including many starts. Based on data, the proposed simple linear empirical model was trained using 75% data and evaluated using 25% data with the mean square error of 10^{-5} or 10^{-6} magnitude. Adapted under the terms of the CC BY license [108]. Copyright 2024, MDPI Energies.

years at 60 °C under following three operation intervals: constant operation with many starts, volatile operation, and mixture of constant and volatile operation, along with starts (see Fig. 9b). The linear structure of the empirical voltage model provided fast computation with good accuracy. Through model fitting, the voltage at a preset reference condition was determined by correcting the voltage measured in real-time. This reference voltage can possibly be used as a novel SoO indicator. The indicator reveals ambiguity with low data coverage; hence a transfer linear regression algorithm was developed. The precision of this empirical model was initially verified using synthetic data. Then, the model was applied to real-world data collected from an industrial electrolyzer mentioned above. Stable SoO estimation was observed by the algorithm. But still, its suitability for long running electrolyzers is unclear. The model is applicable exclusively to electrolyzers operating at moderate current density because of linear relation between voltage and current density. The dominance of non-linear activation overpotential at low current densities necessitates non-linear relationships for these electrolyzers. This indicates that this model is not suitable for other types of electrolyzers, however the model will vary for comparable electrolyzers based on their operational mode. Therefore, to diagnose degradation type of an operating PEMEC, it is indispensable to build degradation model using the data collected from the sensors and to update it regularly as new data becomes accessible. The data training will improve the model reliability in estimating continuous SoO and predicting the RUL with minimal ambiguity. Using this approach, an

algorithm for PEMFC was developed, which presents lifetime prediction with and without incremental learning [131].

5. Conclusion and perspective

In this article, we provide an overview of the ongoing issues through the comprehensive review of the literature, identifying the causes and frequency of failures in PEMEC, as well as operational health monitoring and lifetime prediction. The reproducibility and comparability of degradation rate across different research endeavours remain challenging despite detailed investigations. Regarding this, harmonized protocols outlined by the EU should be implemented with an intent to compare the results and quantitatively assess the target achieved. By publishing the results using an appropriate methodological framework, the worldwide scientific community may use the procedures to formulate a standardized approach for assessing the degradation rate of PEMEC. To date, no study has proposed a method to determine RUL of PEMEC, though fundamental research has been conducted on state-of-health. Therefore, advancing this approach is critical to improving the efficiency and durability of PEMEC systems.

In our view, following are some aspects that should be considered to ensure the reliable evaluation of DR and SoO: The first major issue is the lack of consistency in the design and specification of cell parts and constituents in test benches used by researchers across laboratories. It is critical to collaborate among PEMEC laboratories to establish standard

operating protocols and system hardware for comparable testing. Also, when evaluating the results, it is imperative to consider the history of the system components and the external environmental disturbances. Some of the instances refer to the storage and activation conditions of MEA prior to cell assembly, the cleaning procedures utilized to prepare the cell components, the torque applied to assembly, and the procedure of conditioning MEA post assembly. Additionally, it is necessary to check the quality of other cell components, such as the condition of coatings on the PTL and BPs. MEA failure caused by mechanical damage can also be diagnosed by performing volumetric gas permeability tests and short-circuiting tests. External disturbances may include mechanical vibrations and shocks, electromagnetic interferences, load fluctuations, and other anonymous forms of disturbance. The effective operation of PEMEC requires the regular implementation of preventive measures.

When evaluating SoO, it is important to consider the stringent operating conditions that need an optimal BoP. Multiple sensors need to be used to monitor signals, while a control logic interface should be utilized to govern each subsystem of BoP. This enables continuous monitoring and surveillance using the deployed sensors, which can measure various physico-chemical signals (temperature, water conductivity, pH, gas crossover, FRR, and gas purity) and electrical signals (voltage and internal resistance). By plotting the data across time, a correlation may be developed which facilitates tracking the process of degradation. Therefore, online monitoring using internal sensors has the potential to identify the cause of the voltage rise, although it will undoubtedly raise the cost of the system. This means, state-of-the-art is to diagnose the current degradation state of a running PEMEC through SoO recording. For instance, if SoO tracking over time indicates a continuous degradation of PEMEC, then applying controlled load protocols might recover the electrolyzer at least from reversible losses.

For the above-mentioned experimental approach, a source of operating data is required for training and routine updating of an empirical model. This may effectively quantify the continuous degradation and provide useful data on the SoO of a running PEMEC. This technique might have the potential to develop a global model using a reduced number of health indicators. Industrial electrolyzers, which maybe only utilize voltage as an operational health indicator, might employ this technique. So, extensive studies at the laboratory level must be conducted first, and then applied and modified to systems operating on an

industrial scale. For instance, one must optimize the BoP depending on the electrolyzer's power, since both are proportional. Prognostic methods can be developed based on the reliability of degradation history over time. Effective prediction, both short- and long-term, is of paramount significance to investigate in this respect. To predict lifespan accurately, data filtering approaches must be explored to separate inevitable fault signals from degradation-related signals. Fig. 10 exemplifies the prediction of time to failure of an operating PEMEC, which is based on machine learning models developed by incremental learning of historical data of degradation rate. After the acceptable degradation rate (point C in Fig. 10), preventive maintenance must be required during the predicting phase. Via preventive measures, time to apply overhaul maintenance (point D in Fig. 10) can be determined by the rate at which degradation rate increases exponentially, which includes disassembly of PEMEC and replacement of defective components. For instance, if the degradation rate exceeds the track predicted by machine learning model, immediate steps towards overhaul maintenance should be implemented. In short, preventive and overhaul maintenance can ensure the reliable operation, extended lifespan, and prevention of permanent failure (point E in Fig. 10) of PEMEC.

CRedit authorship contribution statement

Ali Javed: Writing – review & editing, Writing – original draft, Visualization, Investigation, Formal analysis, Data curation, Conceptualization. **Niklas L. Wolf:** Writing – review & editing, Visualization, Investigation. **Fabian Meyer:** Writing – review & editing, Visualization, Investigation. **Leander Treutlein:** Writing – review & editing, Visualization, Investigation. **Hans Kungl:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **André Karl:** Writing – review & editing, Supervision, Project administration. **Eva Jodat:** Writing – review & editing, Supervision, Project administration. **Rüdiger-A. Eichel:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

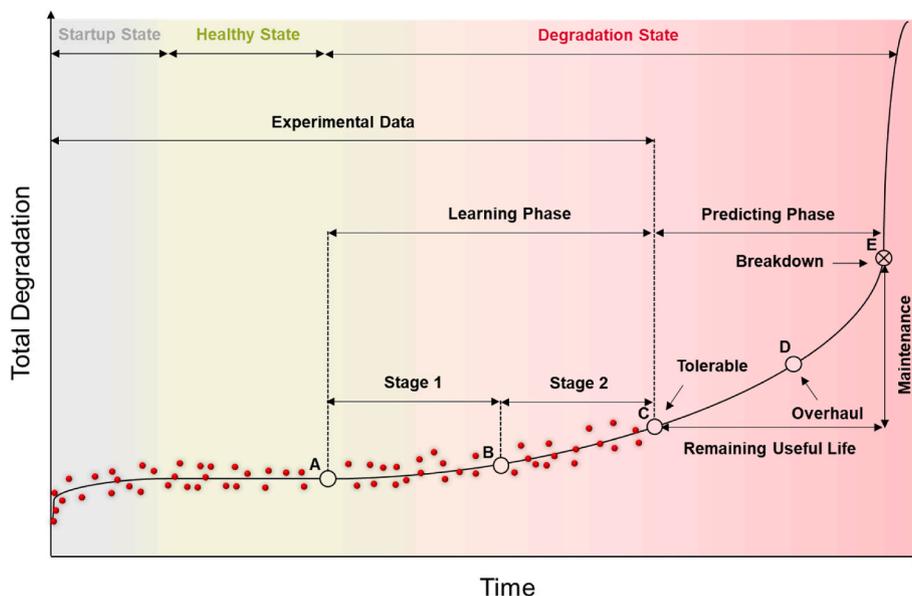


Fig. 10. Illustration of remaining useful life prediction via operational history indicators of a PEMEC during service. Symbol (●) characterizes the mock experimental data. During the learning phase, points A, B, and C represent the instantaneous degradation rate using continuous monitoring. Point C also denotes acceptable or tolerable degradation rate. Point D indicates the overhaul point, which demands the repair or replacement of impaired components of PEMEC. Point E corresponds to the breakdown point, which appeals for prompt shut down of PEMEC to refrain from permanent failure and safety danger.

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