Design of degradation test protocols for a 25 kW PEMFC stack in cogeneration applications

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Abstract:

Proton exchange membrane fuel cells (PEMFC) are a mature technology for high-efficiency combined heat and power (CHP) applications. However, stack durability remains a critical challenge, particularly under dynamic operating conditions representative of real energy demand profiles. While extensive degradation studies have been conducted at cell and short-stack level, there is still a lack of harmonized methodologies for degradation testing at the stack scale, especially for medium-power systems relevant to stationary cogeneration. Moreover, many of the degradation protocols reported in the literature are derived from automotive applications and may not be directly applicable to CHP operating conditions.

This work presents an analysis aimed at identifying, classifying, and structuring the main experimental methodologies currently used to assess degradation in PEMFC stacks. The study is conceived as a preliminary step toward the experimental investigation of a 25 kW PEMFC stack using the newly developed PEMFC stack test bench at the Universidad Politécnica de Madrid (UPM). Rather than focusing on a specific degradation experiment, the contribution of this work lies in the definition of a comprehensive framework to guide future durability testing.

A preliminary literature review is first conducted to identify the most widely used characterization and degradation tests applied to PEMFC stacks. These tests are analysed to determine their specific objectives and their relevance to different degradation mechanisms. For each identified methodology, the following aspects are systematically assessed: type of experimental test, PEMFC components involved, evaluated parameters, execution procedure, required instrumentation, and main conclusions reported in the literature.

Special attention is given to dynamic load cycling protocols proposed as experimental tools to accelerate degradation. The analysis highlights that existing standardized or widely adopted power cycling profiles are primarily oriented toward automotive applications, with limited relevance for stationary cogeneration systems. The lack of representative load cycles for CHP operation is identified as a key gap, motivating the need for adapted testing strategies.

The resulting framework provides a structured reference for the selection and design of degradation tests in PEMFC stacks, supporting the development of robust and application-oriented durability assessment protocols for cogeneration systems.

Keywords:

PEMFC stack, Combined heat and power (CHP), degradation, Accelerated stress test (AST), durability analysis

1. Introduction

In the current landscape of energy generation, cogeneration, also known as Combined Heat and Power (CHP), is a process that enables the simultaneous or sequential generation of electrical and thermal energy from a single system [1], recovering waste heat to achieve overall efficiencies of 80% to 90% [2], [3]. Traditionally, cogeneration systems have been primarily implemented in large-scale power generation plants and industrial facilities. However, in recent years, there has been a growing interest in the development and deployment of CHP systems in residential and commercial environments [2]. This shift is driven by the pursuit of greater energy independence, as observed in Japan, and the need to reduce fuel consumption and pollutant emissions to comply with stringent environmental regulations, such as those enacted by the European Union [4].

Within the context of cogeneration applied to commercial and residential sectors, and to address the aforementioned evolving demands, fuel cells are emerging as the leading alternative to traditional systems due to their high electrical efficiency, ranging from 45% to 60%, their excellent part-load performance, and their capacity to reduce greenhouse gas emissions [5], [6]. Within this technology, proton exchange membrane fuel cells (PEMFCs) stand out for their low operating temperatures, between 60 °C and 120 °C, and short start-up times [4], [7]. These characteristics enable PEM fuel cells to effectively adapt to the daily fluctuations in energy demand typical of these environments [1].

Currently, PEMFCs are the most extensively developed and researched type of fuel cell [1]. Nevertheless, despite their technological maturity, durability remains a critical challenge for their widespread commercial deployment, particularly in applications subject to dynamic operating conditions, such as CHP systems, which impose variable energy demand profiles [1], [8].

To address this durability challenge, current research is focused on understanding the degradation mechanisms that affect fuel cell durability. These studies generally consist of subjecting the fuel cell to durability tests, which can be either steady-state or an accelerated stress test (AST). Steady-state tests generally involve applying constant current density conditions to the fuel cell over extended periods [9], [10]. Alternatively, ASTs enable the application of dynamic load profiles that mimic real-world energy demands within compressed timeframes [10], [11], [12]. During and after these durability tests, specific characterization protocols are conducted to determine the degradation state of the evaluated fuel cell [9]. These characterization techniques are broadly divided into two categories: electrochemical and physical [9], [13].

Despite the widespread use of these testing and characterization methodologies, a significant gap remains in the literature regarding their application to larger-scale systems. While extensive degradation studies have been successfully conducted at the single-cell and short-stack levels, scaling these findings to medium-power systems relevant to stationary cogeneration presents considerable challenges. Furthermore, the majority of the dynamic AST protocols currently reported and standardized in the literature are derived from the automotive sector [14], [15]. These automotive-oriented load cycles entail highly aggressive transients, frequent start-stop events, and operational patterns that are not representative of the specific electrical demand profiles typical of CHP applications [9], [16], [17]. Consequently, there is a critical lack of harmonized testing methodologies and representative load cycles to accurately assess stack durability under realistic stationary cogeneration scenarios.

In response to this limitation, this work presents an analysis aimed at identifying, classifying, and structuring the primary characterization techniques and durability tests currently used to assess degradation in PEMFC stacks. This study is conceived as a fundamental preliminary step toward the future experimental investigation of a 25 kW PEMFC stack, which will be conducted using the newly developed test bench at the Universidad Politécnica de Madrid (UPM).

2. Methodology

To conduct the literature review, two bibliographic searches were performed in the Scopus database: an initial search focused on general degradation studies, and a secondary one centered on degradation in cogeneration systems. Search parameters were consistently restricted to English-language articles published between 2015 and 2026, with results sorted by relevance. The initial search focused on general PEMFC degradation studies ("PEMFC" AND "degradation analysis") and retrieved 1,024 articles. To ensure a concise analysis, this pool was filtered to include only review papers, resulting in a final selection of 64 documents. Subsequently, a targeted search on cogeneration applications ("PEMFC degradation" AND "CHP") returned 27 articles, all of which were comprehensively reviewed. Additionally, pertinent references found within these selected articles were incorporated. The findings derived from this scientific review are presented in the subsequent sections, where the extracted information is systematically structured into three main categories: electrochemical characterization techniques, physical characterization techniques, and durability testing protocols.

3. Degradation analysis via electrochemical characterization

Electrochemical characterization techniques enable the assessment of the efficiency and the evolution of the operating parameters of the evaluated fuel cell [18]. These techniques helps to identify the sources of efficiency loss and understanding the various limiting factors within the system, such as electrochemical reaction kinetics, the ohmic resistance of the components, and mass transport limitations [19], [20]. Although these analysis can be conducted *ex situ* to study the components in isolation, fuel cell evaluations typically rely on *in situ* measurements, as they allow for the assessment of the device state of health and the monitoring of component degradation mechanisms both prior to system start-up and throughout the course of durability testing [21], [22], [23]. Some of the most representative tests are detailed below.

3.1. Polarization curve

The polarization curve, also referred to as the current-voltage (I-V) curve, is the most widely used technique for evaluating the overall performance of a fuel cell under specific operating conditions. Its analysis enables the extraction of crucial operational parameters, such as the open-circuit voltage (OCV), the maximum achievable power density, and the limiting current density [24]. Furthermore, it allows for the variation of different operational parameters, such as the composition, flow rate, temperature, and relative humidity of the reactant gases, in order to analyze their impact on the overall efficiency of the fuel cell [10].

The test involves recording the voltage as a function of current density under a set of constant operating conditions [10], [25], [26]. There are primarily two experimental approaches for obtaining polarization curves. The first is the voltage-controlled method, in which a potentiostat or an electronic load regulates the output potential of the cell while the corresponding current response is recorded. The second is the current-controlled method, which employs a galvanostat or an electronic load to set the output current, recording the resulting voltage evolution as a function of that current [24].

In the context of durability testing, polarization curves are initially obtained prior to the dynamic load cycling and are subsequently recorded at periodic intervals throughout the test. This procedure enables the monitoring of the fuel cell's evolving electrochemical performance and the identification of progressive efficiency losses [27], [28].

Regarding the analysis of the results, a typical polarization curve provides information on fuel cell losses under various operating conditions. At low current densities, activation losses predominate. These are attributed to the rate at which the electrochemical reactions occur and can be minimized by employing effective catalysts [29], [30]. As the current density increases, the voltage drop across the fuel cell escalates, and ohmic losses become significant. These losses stem from the resistance to ionic current flow through the ionomer and the membrane, as well as the resistance to electronic current flow through the gas diffusion layer (GDL), current collectors (CC), and the external circuit [30]. In this region, the voltage drop is predominantly linear [29], [30]. Finally, at high current densities, mass transport effects dominate, and cell efficiency decreases drastically. The limiting factor in this regime is the transport of reactant gases through the porous structure of the support layers and the electrocatalyst layers [29]. Figure 1 illustrates a typical PEMFC polarization curve, identifying the different aforementioned losses associated with the operating current density [20].

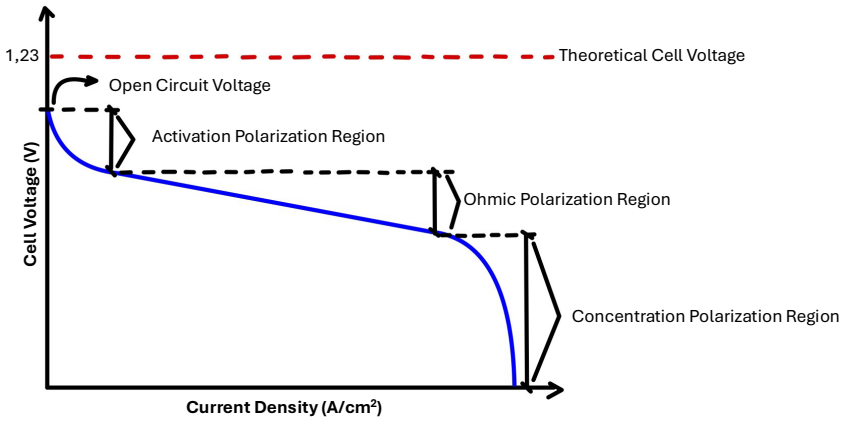

***Figure 1**. PEMFC polarization curve. Source: [20]*

3.2. Electrochemical impedance spectroscopy

Electrochemical Impedance Spectroscopy (EIS), also referred to as alternating current (AC) impedance spectroscopy, is a technique that enables the evaluation of the internal state of the membrane electrode assembly (MEA) and the characterization of the electrode-electrolyte interfaces.

The EIS testing procedure consists of superimposing a harmonic or sinusoidal perturbation onto the system and measuring the resulting impedance across a wide range of frequencies. Experimentally, this is typically carried out using a Frequency Response Analyzer (FRA) coupled with a potentiostat/galvanostat or an electronic load equipped with an AC modulation module. In PEMFC testing, the frequency sweep usually spans from high frequencies down to low frequencies, usually between 0.1 Hz and 10 kHz [31]. Typically, the amplitude of the applied AC signal is set between 5% and 10% of the fuel cell's direct current (DC) operating value [26], [31]. Since a fuel cell exhibits highly non-linear behavior, the small amplitude EIS test allows for the pseudo-linearization of the system response, making it possible to estimate electrical characteristics without significantly altering the system's inherent properties [32]. Furthermore, this test can be conducted in potentiostatic mode, controlling the output voltage, or galvanostatic mode, controlling the output current. In practice, EIS testing is predominantly performed in galvanostatic mode, because a small perturbation in voltage can cause a drastic and non-linear change in current, potentially overloading the cell and the electronic circuits [26], [31], [32], [33].

Executing a full-frequency EIS sweep makes it possible to decouple the simultaneous processes occurring within the fuel cell based on their respective time constants [30]. Although the test results can be represented using Bode plots, they are most commonly visualized through Nyquist plots, which map the imaginary impedance against the real impedance [26], [31]. As illustrated in Figure 2, these plots display the superimposition of different arcs associated with the system's internal resistances. Depending on the evaluated frequency range, they allow for the quantification of the ohmic resistance, charge transfer resistance, and mass transport resistance [33].

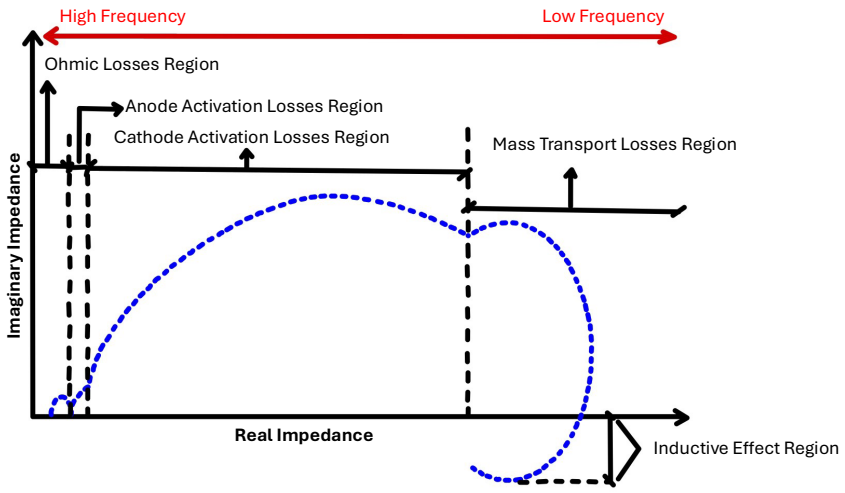

***Figure 2**. Nyquist plot and the different phenomena activated during EIS. Source: [33]*

To extract quantitative physical values from the EIS spectra, the experimental data are fitted using mathematical models. Generally, EIS results are fitted to an Equivalent Electrical Circuit (EEC) composed of resistors, inductors, and capacitors arranged in series or parallel [26], [30]. However, it should be noted that the obtained results are only valid for the specific operating point at which the test was conducted [32]. Despite this limitation, tracking the evolution of the EEC parameters over time remains one of the most powerful diagnostic tools for isolating specific degradation mechanisms during durability testing.

3.3. Cyclic voltammetry

Cyclic Voltammetry (CV) is an electrochemical characterization technique that measures the electrical current flowing through an electrode while cyclically varying the applied electrical potential. Experimentally, this test is executed using a potentiostat. During *in situ* PEMFC testing, the working electrode, typically the cathode, is

purged with an inert gas (N_2) while the counter and reference electrode, typically the anode, is supplied with hydrogen. The potential is then cycled between defined voltage limits at a constant scan rate [30].

The primary objective of conducting cyclic voltammetry is to measure the Electrochemical Active Surface Area (ECSA) of the fuel cell catalyst [30]. The ECSA represents the number of active sites within the catalyst layer that are available for electrochemical reactions to occur [30]. Because the oxygen reduction reaction (ORR) exhibits a significantly higher overpotential than the hydrogen oxidation reaction (HOR) and acts as the overall rate-limiting step, CV tests focus almost exclusively on analyzing the cathode [30]. Generally, a higher ECSA value indicates a more active catalyst [26].

It is worth noting that the quantification of the active area is not obtained directly, but rather by analyzing the distinctive peaks in the resulting voltammogram. These peaks represent processes such as the adsorption and desorption of electrochemically active species, specifically, the hydrogen underpotential deposition region, as well as the oxidation and reduction of platinum [30]. By comparing these voltammograms over time, it is possible to quantify the loss of active catalytic area caused by degradation mechanisms such as platinum dissolution, particle agglomeration, or carbon support corrosion. Figure 3 depicts a typical cyclic voltammogram of a PEM fuel cell cathode before and after a durability test [34].

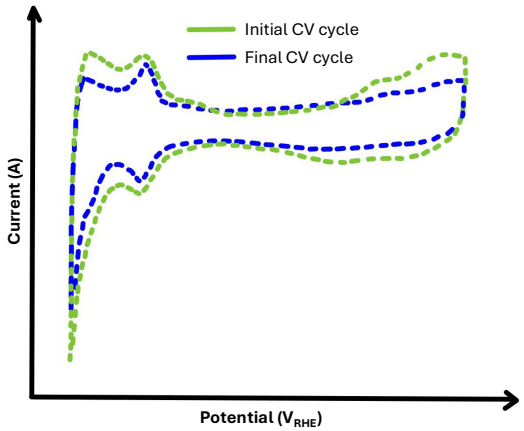

Figure 3. *Typical cycle voltammogram of the cathode before and after a durability test. Source: [34]*

3.4. Linear sweep voltammetry

Linear Sweep Voltammetry (LSV) is an electrochemical characterization technique closely related to cyclic voltammetry. Its fundamental principle consists of applying a potential sweep between a working electrode and a reference electrode while simultaneously monitoring the current generated by the oxidation or reduction of active species at the electrode [26]. Experimentally, like in the CV, this test is performed using a potentiostat. To measure hydrogen crossover in situ, the cathode, working electrode, is purged with an inert gas (N_2), while the anode is supplied with hydrogen. Then a slow linear voltage sweep is applied [25], [26]. The primary methodological difference compared to CV lies in the voltage trajectory: whereas in CV the sweep is bidirectional and cyclic, increasing to a vertex potential and then reversing to complete a cycle, in LSV, the sweep is strictly unidirectional, advancing linearly from an initial potential to a predetermined final potential [25], [26].

In the field of PEM fuel cell characterization, the LSV technique is primarily employed to quantify hydrogen crossover. This phenomenon refers to the undesirable transport of intact hydrogen molecules through the polymer membrane, permeating from the anode to the cathode [26]. Accurately measuring this gas leak is of vital importance in degradation studies, as a progressive increase in the hydrogen crossover limiting current over the stack's lifespan is a direct indicator of membrane degradation [26]. Figure 4 presents a typical graph resulting from an LSV test before and after a durability test.

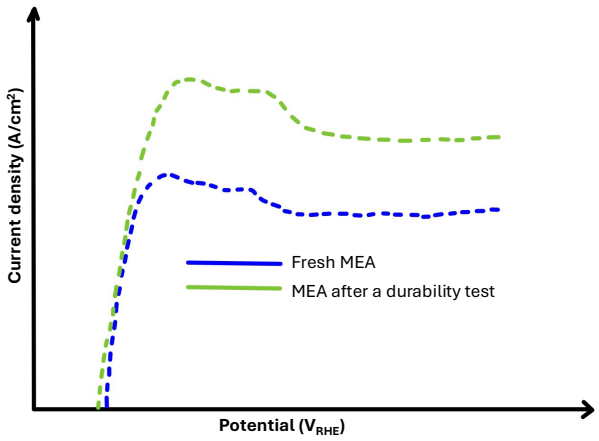

Figure 4. *LSV before and after a durability test. Source: [25]*

4. Degradation analysis via physical characterization

Physical characterization tests are performed prior to and following the application of dynamic load cycling, with the objective of identifying the structural changes that occur within the fuel cell as a consequence of prolonged operation. These analyses are typically conducted *ex situ* once the fuel cell has reached failure or upon completion of the durability test. These are commonly referred to as post-mortem characterization techniques [9], [13]. They enable the evaluation of the physical condition of the internal components, the detection of potential localized failures, and the establishment of direct correlations with the degradation mechanisms observed through electrochemical testing [12]. It is important to note that these procedures can be destructive to fuel cell stacks, as they require the complete or partial disassembly of the stack to extract and analyze individual cells.

4.1. Optical microscopy

The optical microscope, often referred to as a light microscope, utilizes visible light and a system of lenses to magnify images. Optical microscopy has long been employed for the visual analysis of the surface and cross-section of components utilized in PEM fuel cells. Although its resolution is inherently limited by the wavelength of the illumination source, this technique enables the precise measurement of cross-sectional thickness reduction in the Membrane Electrode Assembly (MEA). To achieve this, the post-mortem samples must undergo a rigorous preparation process, which typically involves embedding the MEA in an epoxy resin, sectioning it, and meticulously polishing the exposed surface [11].

This characterization method allows for the observation of the catalyst layer (CL) surface topography, facilitating the identification and classification of interconnected crack formation. These localized failures indicate a structural weakening among the ionomer, the catalyst, and the carbon support as the cell ages [35], [36].

However, standard optical microscopy encounters difficulties when imaging highly transparent samples, such as the proton exchange membrane. To overcome this limitation, advanced optical techniques such as fluorescence, dark-field, and phase-contrast microscopy can be employed [26]. Additionally, when compared to higher-resolution techniques like Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM), optical microscopy is fundamentally restricted by the diffraction limit of light, yielding a maximum resolution of approximately 200 nm [11].

4.2. Scanning electron microscopy

Scanning Electron Microscopy (SEM) is one of the most widely used microscale physical characterization techniques for evaluating the condition of fuel cell components after being subjected to durability tests [29]. The SEM technique is based on scanning a sample with a high-energy electron beam, which enables the acquisition of high-resolution images at the nanometer scale [11], [26], [37].

SEM studies are typically divided into two primary analytical approaches. The first approach consists of analyzing the cross-sectional structure of the MEA to determine the variation in cathode and anode thickness

before and after durability testing [29], [38]. This thickness is often observed to be reduced as a direct consequence of carbon support corrosion [38].

Alternatively, the second approach focuses on investigating the surface morphology of the catalyst layers and identifying changes in the distribution of platinum particles [11], [29], [39].

Finally, to obtain a comprehensive physicochemical characterization, the purely morphological SEM analysis is typically complemented with Energy Dispersive X-ray Spectroscopy (SEM-EDS). This coupled technique allows for elemental mapping and the determination of the exact chemical composition of the materials present both on the surface and within the layers of the MEA [37]. The images and spectra obtained via SEM-EDS are indispensable tools for detecting the presence and accumulation of contaminants derived from structural damage to the cell itself during dynamic operation. Furthermore, they facilitate the evaluation of the degradation state of critical peripheral components, such as the electrode frame and the sealing system, thereby providing a complete overview of the equipment's structural integrity [37].

4.3. Transmission electron microscopy

Transmission Electron Microscopy (TEM) is a technique that enables the physical characterization of fuel cell components at the nanoscale, typically <0.2 nm resolution. By offering a significantly higher resolution than SEM, TEM is positioned as the ideal instrument for accurately determining particle morphology, size, and distribution [11], [26], [29]. This equipment operates at a constant accelerating voltage that can be adjusted according to the specific requirements of each analysis [37].

To conduct the characterization of electrodes via TEM, two primary preparation methods are typically employed [11]. The first method consists of lightly dispersing the catalyst powder onto a thin carbon film. Although this allows for the acquisition of direct information regarding the size and distribution of the catalyst and its support, this approach entails the complete destruction of the electrode's macroscopic structure [11]. The second method involves preparing an intact cross-section of a three-layer MEA using ultramicrotomy with a diamond knife. By preserving the component's architecture, this method is optimal for spatially localizing growing particles within the internal structure following degradation tests [11].

Within the framework of durability testing, the comparison of TEM images taken before and after dynamic load cycling is crucial for quantifying electrocatalyst degradation. Typically, prior to testing, platinum particles exhibit a fine and uniform distribution. However, after prolonged operation, the images reveal a clear growth and agglomeration of these particles [37]. This dimensional increase is a direct indicator that catalyst degradation mechanisms have occurred [11], [26], [29]. Similar to SEM, TEM is frequently coupled with Energy Dispersive X-ray Spectroscopy (TEM-EDS) to track the migration of dissolved platinum ions and the subsequent formation of a "Pt band" within the polymer membrane.

4.4. X-ray diffraction

X-ray Diffraction (XRD) is a physical characterization technique employed to analyze the crystalline lattice structure of fuel cell components, specifically the catalysts and the overall structural integrity of the MEA [16], [29].The underlying physical phenomenon occurs when the wavelength of the incident electromagnetic radiation is comparable to the interatomic spacing within the crystal lattice [29]. This causes the incident X-rays to scatter and reflect off successive parallel planes of atoms. These reflected beams constructively interfere and are detected at specific angles, generating characteristic diffraction peaks [29]. Because the precise position and relative intensity of these peaks are unique to each material, XRD enables the accurate identification of the phase composition and the degree of crystallinity of the analyzed sample [29], [37], [40].

Conducting XRD requires specialized instrumentation, primarily the X-ray diffractometer, which measures the diffraction angles of the scattered beams. A graphite monochromator is often utilized to filter background noise and produce a sharp diffraction pattern, which is subsequently processed using dedicated crystallographic software [16].

Within the context of durability testing, XRD is an indispensable tool for monitoring structural alterations in the catalyst material over time. As a result of fuel cell operation, it is observed that both anodic and cathodic catalysts exhibit a pronounced narrowing of their diffraction peaks, as observed in Figure 5, indicating that the platinum crystallites have grown significantly larger compared to the fresh catalyst [16], [37].Ultimately, this

structural growth confirms the platinum agglomeration processes observed through other techniques, such as TEM, and correlates directly with the loss of ECSA quantified via cyclic voltammetry [16].

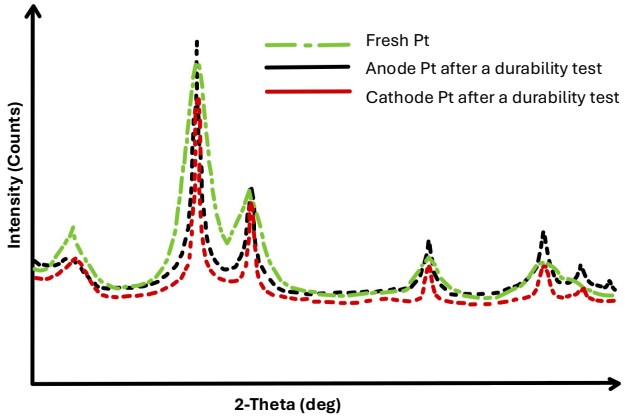

***Figure 5**. XRD patterns obtained for the evaluation of catalyst size after a durability test. Source: [16].*

5. Durability tests

Traditionally, the lifespan analysis of an equipment relies on evaluating its performance under normal operating conditions until failure occurs. Consequently, durability testing methodologies for PEM fuel cells are fundamentally divided into two major categories: steady-state or stationary tests and Accelerated Stress Tests (AST) [10], [11].

5.1. Steady-state durability test

Steady-state tests consist of operating the fuel cell at a constant voltage or current load for thousands of hours to examine the baseline degradation rate of the components [9], [10]. While these tests represent the least aggressive approach and closely mimic nominal continuous operation, they present a critical feasibility issue. For stationary cogeneration applications, the Department of Energy (DOE) target lifespan is established at 40,000 hours [10]. Evaluating a system under steady-state conditions to reach this milestone would require approximately 4.6 years of uninterrupted operation [10]. This makes purely stationary testing practically unfeasible for modern research and development cycles, as it drastically increases experimental time and associated costs, limits sample volume, and requires periodic maintenance stops to recover reversible efficiency losses [9], [10].

5.2. Accelerated stress tests

To overcome the temporal and economic limitations of steady-state testing, the industry and the scientific community heavily rely on Accelerated Stress Tests (AST) [37]. The primary objective of a well-designed AST protocol is to subject the fuel cell to extreme operational conditions, such as high voltages, elevated temperatures, or high current densities, to deliberately and rapidly trigger specific failure mechanisms, minimizing the interference of other system variables [9], [12], [30]. Depending on the specific degradation mechanism targeted for investigation, AST protocols are classified into several subcategories:

- **Start-stop cycling**: This protocol subjects the equipment to alternating and instantaneous charge and discharge phases, inducing severe internal pressure and temperature gradients [38], [41]. The deterioration is primarily caused by the formation of an abrupt hydrogen-air boundary at the anode when the incoming reactant gas comes into contact with residual oxygen during start-up and shut-down transients, leading to severe carbon support corrosion at the cathode [30].

- **Potential cycling**: In this test, the cell voltage is repetitively swept between defined upper and lower limits [41]. This continuous cycling accelerates the electrochemical corrosion of the carbon support and the dissolution of the platinum catalyst, drastically reducing the Electrochemically Active Surface Area (ECSA). Furthermore, it alters the hydration levels of the polymer membrane. The resulting continuous swelling and shrinkage cycles cause severe mechanical fatigue, ultimately leading to pinhole formation, cracking, and delamination [12].

- **Application-specific dynamic load cycles**: To ensure that laboratory ASTs yield results with practical, real-world validity, dynamic load cycles are employed to accurately reproduce actual power demand profiles [37]. Within this category, driving cycles for the automotive sector have been widely studied. There are numerous established standards and protocols in the literature, such as the well-known NEDC cycle, which subject the fuel cell to rapid phases of acceleration, braking, and cruising [14], [15]. Conversely, regarding stationary cogeneration applications, there are currently no universal reference standards or regulations. However, various studies have been conducted employing experimental profiles designed to mimic the variations in thermal and electrical demand across the different seasons of the year (spring, summer, autumn, and winter), thereby allowing for a more realistic approximation of degradation in these specific environments [27], [42].

6. Summary and conclusions

This work has established a comprehensive methodological framework for the design and execution of degradation test protocols in PEMFC stacks, specifically tailored for stationary CHP applications. Driven by the ambitious lifespan target of 40,000 hours required for commercial viability in the cogeneration sector, this review highlights the imperative need to transition from unfeasible steady-state testing to highly representative AST.

Through the systematic analysis of the existing literature, several key conclusions have been drawn regarding the evaluation of PEMFC durability:

- **Synergistic Characterization Approach:** A robust degradation analysis relies on the complementary use of electrochemical and physical characterization techniques. *In situ* electrochemical methods are indispensable for the real-time monitoring of performance decline, allowing for the quantification of activation, ohmic, and mass transport losses, as well as the reduction in Electrochemically Active Surface Area (ECSA) and membrane gas crossover.

- **Post-Mortem Structural Validation:** The electrochemical data must be correlated with *ex situ* physical characterization. Techniques spanning from the microscale to the nanoscale provide physical evidence of the underlying degradation mechanisms.

- **The Gap in Application-Specific ASTs:** While AST protocols such as start-stop and potential cycling are highly effective at isolating specific failure mechanisms, dynamic load cycling remains the most accurate method for evaluating real-world stack lifespan. However, the current scientific landscape is heavily dominated by standardized driving cycles designed for automotive applications. These profiles involve aggressive, short-term transients that fundamentally differ from the long-term, seasonal thermal and electrical demand fluctuations characteristic of stationary CHP systems.

- **Need for Harmonized Cogeneration Protocols:** There is a critical lack of standardized reference cycles for stationary cogeneration, particularly in the medium-power range. Although some preliminary studies have successfully employed seasonal profiles, standardizing these dynamic load cycles is essential to allow for direct cross-study comparisons and the development of effective mitigation strategies.

Ultimately, by identifying, classifying, and structuring these characterization techniques and durability protocols, this study provides a consolidated theoretical foundation. This methodological framework paves the way for the upcoming experimental campaigns, which will focus on applying these dynamic, application-specific degradation protocols to a 25 kW PEMFC stack using the newly developed test bench at the Universidad Politécnica de Madrid (UPM).

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References

[1] H. R. Ellamla, I. Staffell, P. Bujlo, B. G. Pollet, and S. Pasupathi, “Current status of fuel cell based combined heat and power systems for residential sector,” *J. Power Sources*, vol. 293, pp. 312–328, Oct. 2015, doi: 10.1016/J.JPOWSOUR.2015.05.050.

[2] F. Ramadhani, M. A. Hussain, and H. Mokhlis, “A Comprehensive Review and Technical Guideline for Optimal Design and Operations of Fuel Cell-Based Cogeneration Systems,” *Processes 2019, Vol. 7, Page 950*, vol. 7, no. 12, p. 950, Dec. 2019, doi: 10.3390/PR7120950.

[3] A. Perna and M. Minutillo, “Residential cogeneration and trigeneration with fuel cells,” *Current Trends and Future Developments on (Bio-) Membranes: Cogeneration Systems and Membrane Technology*, pp. 197–239, Jan. 2020, doi: 10.1016/B978-0-12-817807-2.00009-5.

[4] A. Ozawa and Y. Kudoh, “Performance of residential fuel-cell-combined heat and power systems for various household types in Japan,” *Int. J. Hydrogen Energy*, vol. 43, no. 32, pp. 15412–15422, Aug. 2018, doi: 10.1016/J.IJHYDENE.2018.06.044.

[5] B. C. Tashie-Lewis and S. G. Nnabuife, “Hydrogen Production, Distribution, Storage and Power Conversion in a Hydrogen Economy - A Technology Review,” *Chemical Engineering Journal Advances*, vol. 8, p. 100172, Nov. 2021, doi: 10.1016/J.CEJA.2021.100172.

[6] C. Zhu *et al.*, “Research status and advances of ammonia and hydrogen in the field of energy: Combined utilization,” *Energy Convers. Manag.*, vol. 327, p. 119610, Mar. 2025, doi: 10.1016/J.ENCONMAN.2025.119610.

[7] T. Elmer, M. Worall, S. Wu, and S. B. Riffat, “Fuel cell technology for domestic built environment applications: State of-the-art review,” *Renewable and Sustainable Energy Reviews*, vol. 42, pp. 913–931, Feb. 2015, doi: 10.1016/J.RSER.2014.10.080.

[8] V. Cigolotti, M. Genovese, and P. Fragiacomo, “Comprehensive Review on Fuel Cell Technology for Stationary Applications as Sustainable and Efficient Poly-Generation Energy Systems,” *Energies 2021, Vol. 14, Page 4963*, vol. 14, no. 16, p. 4963, Aug. 2021, doi: 10.3390/EN14164963.

[9] X. Z. Yuan, H. Li, S. Zhang, J. Martin, and H. Wang, “A review of polymer electrolyte membrane fuel cell durability test protocols,” *J. Power Sources*, vol. 196, no. 22, pp. 9107–9116, Nov. 2011, doi: 10.1016/J.JPOWSOUR.2011.07.082.

[10] Y. Wang, K. S. Chen, J. Mishler, S. C. Cho, and X. C. Adroher, “A review of polymer electrolyte membrane fuel cell durability for vehicular applications: Degradation modes and experimental techniques,” *Energy Convers. Manag.*, vol. 199, no. 4, p. 112022, Nov. 2019, doi: 10.1016/j.apenergy.2010.09.030.

[11] J. Zhang, H. Zhang, J. Wu, and J. Zhang, “Fuel Cell Degradation and Failure Analysis,” *Pem Fuel Cell Testing and Diagnosis*, pp. 283–335, 2013, doi: 10.1016/B978-0-444-53688-4.00011-5.

[12] M. Bampaou, D. Georgiou, K. Papaioannou, and K. D. Panopoulos, “Post-mortem analysis as a method to identify degradation of PEM fuel cells affecting their durability in maritime applications,” *Int. J. Hydrogen Energy*, vol. 177, p. 151574, Oct. 2025, doi: 10.1016/J.IJHYDENE.2025.151574.

[13] T. Ma *et al.*, “Recovery characteristics of reversible degradation for proton exchange membrane fuel cell stack under accelerated stress test,” *Chemical Engineering Journal*, vol. 493, p. 152549, Aug. 2024, doi: 10.1016/J.CEJ.2024.152549.

[14] P. Thiele, Y. Yang, S. Dirkes, M. Wick, and S. Pischinger, “Realistic accelerated stress tests for PEM fuel cells: Test procedure development based on standardized automotive driving cycles,” *Int. J. Hydrogen Energy*, vol. 52, pp. 1065–1080, Jan. 2024, doi: 10.1016/J.IJHYDENE.2023.08.292.

[15] G. TSOTRIDIS, A. PILENGA, M. G. DE, and T. MALKOW, “EU HARMONISED TEST PROTOCOLS FOR PEMFC MEA TESTING IN SINGLE CELL CONFIGURATION FOR AUTOMOTIVE APPLICATIONS,” 2015, doi: 10.2790/342959.

[16] R. L. Borup, J. R. Davey, F. H. Garzon, D. L. Wood, and M. A. Inbody, “PEM fuel cell electrocatalyst durability measurements,” *J. Power Sources*, vol. 163, no. 1, pp. 76–81, Dec. 2006, doi: 10.1016/J.JPOWSOUR.2006.03.009.

[17] F. Nandjou, J. P. Poirot-Crouvezier, M. Chandesris, J. F. Blachot, C. Bonnaud, and Y. Bultel, “Impact of heat and water management on proton exchange membrane fuel cells degradation in automotive application,” *J. Power Sources*, vol. 326, no. 2, pp. 182–192, Sep. 2016, doi: 10.1016/j.jpowsour.2016.07.004.

[18] M. Mohsin, R. Raza, M. Mohsin-ul-Mulk, A. Yousaf, and V. Hacker, “Electrochemical characterization of polymer electrolyte membrane fuel cells and polarization curve analysis,” *Int. J. Hydrogen Energy*, vol. 45, no. 45, pp. 24093–24107, Sep. 2020, doi: 10.1016/j.ijhydene.2019.08.246.

[19] F. Wang *et al.*, “Stack-level diagnosis of proton exchange membrane fuel cell by the distribution of relaxation times analysis of electrochemical impedance spectroscopy,” *J. Power Sources*, vol. 603, no. 4, p. 234420, May 2024, doi: 10.1016/j.xinn.2021.100180.

[20] T. A. Arslan and H. Bayrakçeken, “A Comprehensive Review on Fuel Cells: From Fundamental Principles to PEM Fuel Cell Membranes,” *Engineering Perspective*, vol. 5, no. 4, pp. 194–222, Dec. 2025, doi: 10.64808/engineeringperspective.1791743.

[21] K. A. Kasuk, J. Nerut, V. Grozovski, E. Lust, and A. Kucernak, “Design and Impact: Navigating the Electrochemical Characterization Methods for Supported Catalysts,” *ACS Catal.*, vol. 14, no. 16, pp. 11949–11966, Aug. 2024, doi: 10.1021/acscatal.4c03271.

[22] L. Möller, M. Rink, H. Kemmer, and T. von Unwerth, “Comparing PEMFC state-of-health characteristics obtained by Galvanostatic Charge Method with and without nitrogen flush,” *J. Power Sources*, vol. 622, no. 5, p. 235366, Dec. 2024, doi: 10.1016/j.jpowsour.2024.235366.

[23] I. Hartung, S. Kirsch, P. Zihrul, O. Müller, and T. Von Unwerth, “Improved electrochemical in-situ characterization of polymer electrolyte membrane fuel cell stacks,” *J. Power Sources*, vol. 307, no. 3, pp. 280–288, Mar. 2016, doi: 10.1016/j.jpowsour.2015.12.070.

[24] K. Jiao *et al.*, “Experimental characterization and diagnostics,” *Water and Thermal Management of Proton Exchange Membrane Fuel Cells*, pp. 67–120, 2021, doi: 10.1016/B978-0-323-91116-0.00003-1.

[25] D. Seo, J. Lee, S. Park, J. Rhee, S. W. Choi, and Y. G. Shul, “Investigation of MEA degradation in PEM fuel cell by on/off cyclic operation under different humid conditions,” *Int. J. Hydrogen Energy*, vol. 36, no. 2, pp. 1828–1836, Jan. 2011, doi: 10.1016/J.IJHYDENE.2010.02.053.

[26] J. Zhang, H. Zhang, J. Wu, and J. Zhang, “Techniques for PEM Fuel Cell Testing and Diagnosis,” *Pem Fuel Cell Testing and Diagnosis*, pp. 81–119, 2013, doi: 10.1016/B978-0-444-53688-4.00003-6.

[27] R. Chattot and S. Escribano, “Ageing studies of a PEM Fuel Cell stack developed for reformate fuel operation in µCHP units: Development of an accelerated degradation procedure,” *Int. J. Hydrogen Energy*, vol. 40, no. 15, pp. 5367–5374, Apr. 2015, doi: 10.1016/J.IJHYDENE.2015.01.066.

[28] T. Chu *et al.*, “Degradation analysis of the core components of metal plate proton exchange membrane fuel cell stack under dynamic load cycles,” *Int. J. Hydrogen Energy*, vol. 47, no. 11, pp. 7432–7442, Feb. 2022, doi: 10.1016/J.IJHYDENE.2021.12.068.

[29] G. Hinds, “Performance and Durability of PEM Fuel Cells: A Review,” 2004.

[30] A. Broer, H. Polinder, and L. van Biert, “Polymer electrolyte membrane fuel cell degradation in ships — Review of degradation mechanisms and research gaps,” *J. Power Sources*, vol. 640, p. 236678, Jun. 2025, doi: 10.1016/j.jpowsour.2025.236678.

[31] S. M. Rezaei Niya and M. Hoorfar, “Study of proton exchange membrane fuel cells using electrochemical impedance spectroscopy technique – A review,” *J. Power Sources*, vol. 240, no. 7, pp. 281–293, Oct. 2013, doi: 10.1016/j.jpowsour.2013.04.011.

[32] M. Becherif, H. S. Ramadan, K. Cabaret, F. Picard, N. Simoncini, and O. Bethoux, “Fault detection and isolation of high temperature proton exchange membrane fuel cell stack under the influence of degradation,” *J. Power Sources*, vol. 359, pp. 37–47, Aug. 2017, doi: 10.1016/j.egypro.2015.07.629.

[33] N. V. Dale, M. D. Mann, H. Salehfar, A. M. Dhirde, and T. Han, “Ac impedance study of a proton exchange membrane fuel cell stack under various loading conditions,” *J. Fuel Cell Sci. Technol.*, vol. 7, no. 3, pp. 0310101–03101010, Jun. 2010, doi: 10.1115/1.3207871.

[34] S. J. C. Cleghorn *et al.*, “Ex-situ and in-situ degradation studies of MEAs used in 1 kW PEM fuel cell stack,” *Int. J. Hydrogen Energy*, vol. 48, no. 25, pp. 9426–9435, Mar. 2023, doi: 10.1016/s0360-3199(97)00016-5.

[35] S. Shin, J. Kim, S. Lee, T. Ho Shin, and G. A. Ryu, “Multimodal Data-Driven Prediction of PEMFC Performance and Process Conditions Using Deep Learning,” *IEEE Access*, vol. 12, pp. 168030–168042, 2024, doi: 10.1109/ACCESS.2024.3472849.

[36] J. H. Wee, “Impact of electrode thick spot irregularities on polymer electrolyte membrane fuel cell initial performance,” *J. Power Sources*, vol. 466, no. 8, p. 228344, Aug. 2020, doi: 10.1016/j.rser.2006.01.005.

[37] B. Li *et al.*, “Durability degradation mechanism and consistency analysis for proton exchange membrane fuel cell stack,” *Appl. Energy*, vol. 314, p. 119020, May 2022, doi: 10.1016/J.APENERGY.2022.119020.

[38] Z. Liu, H. Chen, and T. Zhang, “Review on system mitigation strategies for start-stop degradation of automotive proton exchange membrane fuel cell,” *Appl. Energy*, vol. 327, p. 120058, Dec. 2022, doi: 10.1016/J.APENERGY.2022.120058.

[39] J. You *et al.*, “Porous Carbon Supports for Low-Pt Proton-Exchange Membrane Fuel Cells,” *Electrochemical Energy Reviews 2025 8:1*, vol. 8, no. 1, pp. 22-, Nov. 2025, doi: 10.1007/S41918-025-00259-8.

[40] M. Obermaier, M. Rauber, A. Bauer, T. Lochner, F. Du, and C. Scheu, “Local Fuel Starvation Degradation of an Automotive PEMFC Full Size Stack,” *Fuel Cells*, vol. 20, no. 4, pp. 394–402, Aug. 2020, doi: 10.1002/FUCE.201900180.

[41] G. TSOTRIDIS, A. PILENGA, M. G. DE, and T. MALKOW, “EU HARMONISED TEST PROTOCOLS FOR PEMFC MEA TESTING IN SINGLE CELL CONFIGURATION FOR AUTOMOTIVE APPLICATIONS,” 2015, doi: 10.2790/342959.

[42] E. Pahon *et al.*, “Long-term tests duration reduction for PEMFC µ-CHP application,” *Int. J. Hydrogen Energy*, vol. 42, no. 2, pp. 1527–1533, Jan. 2017, doi: 10.1016/j.ijhydene.2016.06.222.