Influence of Cycle Repetition on Stack Voltage Degradation during Fuel Cell Stress Tests

R. Yeetsorn[1,*], R. Petrone[2], D. Hissel[3], F. Harel[3], E. Breaz[3], F. Gao[3], M.C. Pera[3]

[1]The Sirindhorn International Thai-German Graduate School of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand

[2]LUSAC Laboratory (EA4253), Caen Normandy University, 50100, Cherbourg-en-Cotentin, France

[3]FCLAB, CNRS, Univ. Bourgogne Franche-Comte, rue Thierry Mige, F-90010 Belfort Cedex, France

FEMTO-ST, CNRS, Univ. Bourgogne Franche-Comte, Belfort, France

[*] Corresponding author: rungsima.y@tggs.kmutnb.ac.th

Abstract

A voltage decrease in long-term operation of hydrogen fuel cell electric cars under steady settings under constant load and dynamic operating conditions is a performance constraint in concern. Although, accelerated stress test (AST) procedures have been seek to diagnose degradation, the AST results of fuel cell stacks have not been reported extensively. The purpose of this paper was to discuss the generation of AST of fuel cell stacks based on real load profiles and the consequences of load changes and start-stop circumstances, which are mostly generated by common driven cycles in urban regions with high driving speeds and traffic jams. The highlight of this study is to analyze the effects of cycle repetition on the fuel cell stack ageing, especially, voltage degradation factor, degradation kinetics, and energy consumption. The relation between actual system temperatures in side cells assembled in the fuel cell stacks and materials degradation was also analyzed. Results presented high heat accumulation, related to chemical degradation, occurred during load cycling, and it may result in membrane thinning and pinholes in the membrane. Temperature cycling corresponded to mechanical degradation generated during the start-stop cycling test, and that may lead to membrane degradations; cracking, tearing, and pinholes.

Keywords: PEMFC stack, Accelerated stress test for PEMFC stack, Cycle repetition, Load profile, Voltage degradation, Load cycling, Start-stop cycling, Temperature cycling

1 Introduction

Automotive manufacturers have paid attention to electric vehicles (EV) which is a vehicle that uses one or more electric motors or traction motors for propulsion since they will be implemented in the transition of the transportation sector to environmentally friendly light-duty vehicles. Examples of EVs on the road today are a hybrid electric vehicle (HEV), plug-in hybrid electric vehicle, battery electric vehicle (BEV), and fuel cell electric vehicle (FCEV) [1]. FCEVs use proton exchange membrane fuel cells (PEMFCs) as electric converters and operate mostly using compressed hydrogen. During the operation, FCEVs are quiet and produce no emissions similar to a BEV, but their refilling time is significantly reduced. Considering an EV providing 85 kWh energy storage, FCEV can be refueled in about 5 min, meanwhile, a battery pack boasting a rate of 120 kW requires at least 40 min for a full charge from full depletion [2]. In this scenario, PEMFC can be implemented in the transition of the transportation sector to environmentally friendly heavy and light-duty vehicles, and operated under dynamic working conditions or constant load in steady conditions [3], depending on the EV level of hybridization. Dynamic driving cycles are composed of sudden load variations, start-stop repetitions, several load values among idle running, full power running, overload running conditions, cold starting [4]. Thus, the performance of FCEVs corresponds to driving conditions in different application behaviors. The integration of stability and durability decay rates, which occur during continuous and uninterrupted operation, is measured as a total performance degradation rate. For most fuel cell applications, a degradation rate less than 0.3-500 $\mu V\ h^{-1}$ per cell is desired or lower than 10% loss in fuel cell efficiency at the end of the test (EoT) [5]. The most prominent factor influencing performance degradation in PEMFC is the degradation of main component materials incorporated with rapid changes and severe operational conditions. This would have dramatic effects on the requirements for long lifespan, which are considered to be operational hours. Table 1 illustrates the relation among driving behaviors, operating conditions, and degradation characteristics of the main components of PEMFC. Membrane [6], catalyst [7-10], gas diffusion layer (GDL) [11], and bipolar plates (BPs) [11], main fuel cell components, principally affect the PEMFC performance. The membrane with a catalyst layer is the most imperative component of a PEMFC, and it has tasks in order to work properly; generate a redox reaction with high reaction rate, separate fuel and oxidant, electrically insulate the anode from the cathode, and conduct protons from anode to cathode. Changes in the membrane characteristics reducing the capability to fulfil the tasks will reduce the electrochemical reactions occurring in the PEMFC leading to kinetics degradation. Membrane degradation takes place as both physical thinning and as loss in ionic conductivity of a membrane, and both cases influence the fuel cell performance damagingly. It is usual to classify the membrane degradation into three categories: mechanical, thermal, and chemical/ electrochemical degradations such as peroxide and hydrogen peroxide production, hydrogen and air crossover [12]. Congenial membrane defects or unfitting membrane-electrode assembly (MEA) fabrication causes perforations, cracks, tears, or pinholes which are mechanical degradation affecting primary cell life failure. The overall dimensional changes during various operating conditions owing to non-humidification (low humidification and relative humidity cycling) are also harmful to mechanical durability [13]. In terms of thermal degradation, membrane protonic conductivity decreases considerably with the decrease in water content, when the fuel cell is operated at high temperatures and under low humidity [14]. Chemical or electrochemical degradation of the membrane involves many reasons such as highly exothermal combustion between H_2 and O_2 [15]. Operating temperatures higher than 80°C result in the mechanical degradation of the membrane because the glass transition temperatures of perfluorosulfonic acid (PFSA) membranes are approximately 80^{o}C [16]. Degradation rates also increase with increasing rates of oxygen reduction reaction for temperatures up to 80^{o}C [17]. High temperature brings about the chemical/electrochemical membrane degradation leading to pinholes on the membrane that affect the gas crossover, fluoride-ion emission, and ion exchange capacity [18]. The catalyst degradation is a foremost source of FC performance deterioration, and changes in catalyst characteristics impacting FC performance are a detachment of catalyst particles from carbon support, Ostwald ripening of particles, agglomeration and associated growth or sintering of particles, and dissolution of the catalyst [19]. The Ostwald ripening and sintering of catalyst particles happen under high accumulated temperature and voltage cycling conditions. This phenomenon begins with the dissolution of smaller particles and the growth of larger particles [20]. A chemical reaction on the anode and cathode catalysts can also produce peroxide and hydroperoxide radicals reasoning to a chemical attack on the membrane and catalyst layer [21-22]. Another important source of deterioration is the change in mass transport inside the porous component such as gas diffusion layers (GDLs). The gas transport and water management inside GDLs can be severely affected when the GDL degradation occurs. In a scenario of degradation in the gas diffusion layer (GDL), high temperature and long-term run may convert a hydrophobic GDL surface to a hydrophilic surface, and this spectacle hinders gas convection and diffusion [23]. Furthermore, GDL has an opportunity to be oxidized in an acid atmosphere. How to maintain superior properties of bipolar plates, the significant component of PEMFC, consisting of uniform gas distribution, good water management, lower pressure drop, higher power density, lower cost, high mechanical strength, and easy fabricating, has become a technical challenge for PEMFC performance improvement. Thus, a vital challenge facing this target is limited durability of bipolar plates. Bipolar plate degradation is mostly due to corrosion problems in an acid circumstance long-time operation [24]. This paper aims to link the PEMFC performance losses induced by the driving cycles' profiles, their variation concerning the adopted strategy for power management and the development of an accelerated stress test protocol-oriented real load profiles.

In the case of FCEV, the resulting load profile is mainly used to study the FC operations and degradations and the related hydrogen consumptions [25-26]. Because driving conditions can differ among regions, standard driving cycles have been designed by organizations to compare the performances of different vehicles. Particularly, driving cycles can be composed of two major parts: steady-state and transient cycles. The steady-state driving pattern analyzes vehicle behavior under constant speed, whereas the transient type captures the temporary behavior during actual driving. During the years, several driving cycles have been modified *via* different methodologies regarding driving specifications, such as cycle duration, speed, number of stops, acceleration and deceleration, and certain city environments [26-27]. To study, the load profile impact in both mechanical and electrochemical FC degradations mechanisms newer load cycles started to couple start-stop cycling, high dynamics, idling and full power conditions with different stress factors, such as temperature and relative humidity cycles [28-33].

Depending on load dynamics and overload values, the PEMFC could be limited for transient peak power demand, which in the case of a high-power system under various operating conditions will impose the FC oversizing or in any case confines the PEMFC operations [34]. If this dynamic is not respected (the external load changes promptly), reactants would not be delivered in time and the FC cell will operate in starvations conditions. Furthermore, water and thermal management are also affected by severe load changes [35]. Load cycling test protocols are particularly used to analyze the impact of the load variations on the FC operating conditions and performance, including the reactants' mass flows, humidification levels, and temperature [36].

The major sources of the decrease in voltage performance were fuel starvation conditions, generating carbon corrosion and Pt particle migration and agglomeration. Cyclic current loading conditions simulating the real road driving were operated for a total of 1,000 h by Liu et al. [37]. The results exhibited that mass transport limitations were identified as the major degradation source. Ohyagi et al. [38] performed load cycling tests (50,000 cycles) at high relative humidity conditions at 91^{o}C to examine the durability of the catalyst. In parallel, the Federal test procedure (FTP)-75 driving cycle [39] was operated to study the dynamic behavior of the PEMFC in fuel cell hybrid vehicles. However, a less intrusive FC load demand can be obtained in the case of HEV through a suited power management optimization. The resulting load profiles are then composed of step-by-step load variations at controlled and lower dynamics (quasi-static profiles) [40-45]. The start-stop procedures are also a sensible point to concern for a PEMFC automotive application, since repeated start-stop procedures can generate both temperature and humidity cycles [46-47]. In these conditions the MEA will experience repeated swelling and contraction processes, generating mechanical stress-strain variations [48]. Moreover, improper start and stop conditions are also the causes of starvation conditions and local gas mixture existing at the anode side [49]. These features generate high cathode potential causing radical carbon corrosion, the catalyst particle sintering and dissolution. The start-stop cycling resulted in high degradations of the MEA at different areas, particularly an important reduction of the electrochemical surface area (ECSA) and the catalyst support corrosion phenomena were observed [50]. In analogy to the low-temperature PEMFC, the ECSA reduction and the carbon corrosion phenomena resulted in major degradations. Qiu et al. [51] decided to couple the effects of both start and stop conditions to relative humidity cycles setting a specific relative humidity start-stop cycling procedure (RH-start-stop). Both mechanical and electrochemical stresses were investigated. If improper load variations and start and stop conditions appears as the most critical conditions, however, some voltage recovery can be correlated to an interruption in a fuel cell continuous operation. Particularly, a voltage recovering can be observed after an operation interruption such as an operation restarting (start-stop procedure), in-situ characterizing, or gas flow changing [52-54]. Through the stop procedure, the interruption of the air feeding decreases the cathode potential, reversing the platinum oxidation phenomenon [53]. An interesting issue was found that the performance recovery progressively rises with increasing the duration of the interruption. However, it is worth underlining that voltage recovery can also relate to current density, thermal management and water management. The relations among these conditions can impact Pt catalyst utilization, membrane conductivity, and electrode kinetics [55-56].

Automotive applications require more than 5,000 h of fuel cell lifetime, while residential applications need longer than 20,000 h [55]. To enhance the PEMFC lifetime the "a priori" knowledge of the MEA degradation is required. Several works have been performed to study the FC degradations' mechanisms [6, 44-45], however, these studies usually resulted in expensive long test campaigns. The accelerated stress test (AST) protocols have been then introduced for exploring the cell degradation behavior in a short time [56]. Different stress factors can accelerate the degradation processes of PEMFCs, including heat and humidity, potential and start and stop cycling. A direct correlation between the results of the degradation tests and the real load profile was addressed as the following examples. A real electric bus load cycle was analyzed by Chen et al. [33] and separated into different sub-cycles, isolating both load cycling, start-stop, idling and overload conditions [33]. Each sub-cycle was subsequently reproduced in a laboratory to evaluate the respective FC degradation ratio. The combination of the experimental activity results given FC ageing effects similar to the voltage degradation observed in a real application. In the accelerated load cycling test (ALC) procedure [9] the actual load cycle profile is converted in as simple as possible sub-cycles, for which the RMS value of the actual load profile is conserved. Overload conditions and start-stop repetitions are also considered. Subsequently, both the amplitude and the number of repetitions of the obtained sub-cycles are increased proportionally with the load dynamics. During the protocol setup, the first step was aimed to identify the main stressors involved in the reference profile, such as the load dynamics and the start-stop repetitions. If PEMFCs start up and shut down intermittently, the cell temperature, humidity level, gas flow rate and local gas makeup are dissimilar from steady-state conditions [49-50]. The hydrogen/air interface or local gas mixture existing at the anode is a major characteristic during start-up and shut down steps [51]. This feature gives high cathode potential causing radical carbon corrosion, catalyst particle sintering, catalyst particle removal from a catalyst supporter and dissolution in an electrolyte. Differentiations in reactant flow rates and water content lead to the wetting and drying processes of the MEA component inside a PEMFC. The MEA will experience repeated swelling and contraction processes, and it implies that MEA will encounter mechanical stress-strain variations. In other words, thermal and hydration change throughout intermittent start-stop mode induce mechanical stresses [52].

2 Experimental

2.1 PEMFC Specification

Two commercially available fuel cell stacks used for all experimental activities are PM-200-12-V4 PEMFC stacks (Proton Power Fuel Cell GmbH). Each stack contains 12 single cells that are practically stacked together to give 1 kW of power. The stacks are typically operated with air and pure hydrogen, and a liquid cooling system is provided for the stack operation. These stacks were assembled with commercially available membranes, gas diffusion layers and machined graphite flow bipolar plates. The nominal specifications of both PEMFC stacks used in this research work are provided in Table 2.

2.2 Operating Condition

The operating temperature was maintained at 55°C under dry reactant gases. Stoichiometry of hydrogen gas (H_2) and the air was validated according to an operating instruction of PM200. Flow rates of H_2 and air were imposed by the software operating controller corresponding to H_2 and air stoichiometry and operating load current. Other operating conditions were shown in Table 3. The polarization characteristics were periodically evaluated using an electric load (Dynaload RBL100-300-2000). Moreover, the potential of single cells was also observed along experimental properties to observe the influence of single-cell degradation on stack degradation behavior. The parameters and studied factors, such as current, stack voltage, single cell voltage, pressure, temperature, inlet and outlet flows, etc., were controlled and monitored through interface controllers (National instrument interface) which developed from Labview™. Measurement sensors, located at different position of the test station, have a ±0.001-unit range of reported data.

2.3 Load Profile Design

The major goal of creating this profile was to look into how driving behaviors affect FC stack performance to enable the development of small urban FCEVs like product delivery vehicles that help with e-commerce growth. The power demand interval in the cyclic profile is allocated to an urban cycle's power demand. The start-stop cycle accounts for the possibility of frequent start-stop situations during the delivery procedure. As a result, evaluating the impact of start and stop repetition may be the best technique in this situation. The first stack was run under the operating condition maintained in the aforementioned section as a reference profile. The part aims to observe the effects of the quasi-static load profile on PEMFC degradation. This quasi-static reference profile was developed to separately investigate the impacts of stationary conditions, load variations, and start-stop conditions on the stack voltage degradation. The reference profile was schematized in Figure 1 (A) and Table 4. Preconditioning and stack warming-up methods were completed 24 h before the beginning of the test (BoT) measurements, polarization behavior and electrochemical impedance spectra. The PEMFC stack was characterized through sequential polarization curves in both current-increasing (from 0 A to 130 A) and decreasing (from 130 A to 0 A) directions to observe the hysteresis between the I-V curves. The same measurements were carried out at the beginning and the end of stack life. After BoT, the stack was constantly operated at 70 A (according to average power) for 24 h to study the effect of the stationary condition on stack voltage changes. This stationary condition was carried out one time before starting the new load cycling conditions. The load cycle was started to operate after the stationary conditioning, and each load cycle was run from 20 A, which was a minimal constant-current operating value, to the high current value of 100 A. This range was set considering the current densities values commonly solicited during a driven cycle. Moreover, a middle step was fixed at the average power operations, corresponding to 70 A. A sequence of 10 repetitions in 24 h was imposed for the load cycles, and then the characterization of the stack polarization behavior was scheduled for 360 h or 15 days. The start-stop cycling test was individually run with 10 cycles per 24 h, and a measurement window was also scheduled every 24 h. H_2 and air were not supplied when the start-stop current was cut off. At this duration, the stack system was naturally cooled down. A period of 75 min for cooling was considered during the system off. However, problems of water saturation and flooding may occur and they should be eliminated before restarting the PEMFC system. In this experiment, reactant gases were ventilated before the load shut-down step and the reactant shut-off process were manipulated. In analogue, reactants were fed before applying electrical load at a stoichiometric factor corresponding to drawing current at 20 A. The start-stop cycling test was continuously operated for 360 h. Afterwards, the end of the test (EoT) was analyzed. In brief, 150 load and 150 start-stop cycles were introduced to the process of the reference profile. Note that the cycles were carried out with 1 A s^{-1} of a current ramp. The reference single cycle interval was fixed approximately 140 min. The interval corresponds to normal vehicle utilization to go for daily work and to go back, and this would also relate to using vehicles for other activities in the evening. The next part of the work was the accelerated stress test. The accelerated profile was, created by analogy with the reference cycling profile. Note that this test was conducted using the second stack. The accelerated profile resulted in increasing the number of single cycles repetitions. The repetitions in the accelerated cycle profile were increased from 10 (in reference profile) to 50 repetitions for each day according to the accelerated load cycle (ALC) protocol [53]. Therefore, 50 repetitions per day were applied in both load cycling and start-stop cycling. The influences of the accelerated profile on voltage degradation, voltage rate variation, and polarization behaviors induced by load and start-stop cycling, were analyzed. The adopted accelerated stress cycle is illustrated in Figure 1 (B) and Table 4. The same protocol adopted for the reference profile is applied. Consequently, 15 days were scheduled both for load cycling and start/stop repetitions, respectively. In this configuration 750, load and 750 start-stop cycles were introduced, instead of the 150-repetition applied in the reference profile.

3 Results and Discussions

3.1 The Primary Investigation on Speed Variation Used for a Stress Test Profile

During a driving cycle, a vehicle is propelled at various speeds as a dynamic process. At high-speed driving, PEMFCs must generate a high current to propel the vehicle, and then severe circumstances leading to material degradation may occur. For a better understanding of the idea of setting driving speed variation in the stress test profile, the electrochemical impedance spectroscopy (EIS) technique was used for preliminary observation. The EIS is a diagnostic tool based upon system dynamics since the resulting impedance of the system can be measured in a wide range of frequencies. Figure 2 illustrates the electrochemical behavior occurring in galvanostatic mode at 20, 70, 100, 120, and 130 A. The voltage of single cells at each operation were 0.63, 0.40, 0.30, 0.25, and 0.20 V respectively. These current values were used for the investigation because they are in the range of production capacity of the PEMFC stack. Furthermore, the values were used for designing the driving profile as mention in the experimental methodology section. Throughout redox reaction in a PEMFC operation, different chemical and electrochemical reactions typically happening on the electrode surface, concentration gradient, or mass transport hindrance influence the PEMFC performance [54]. It implies that those parameters impact material damaging that one of the main causes to reduce the stack performance. At a high-frequency range of Nyquist plots, the resistance of the PEMFC stack can be determined, while the double-layer charging and charge transfer reactions can be observed at the low-frequency range [55]. Moreover, diffusion processes can be observed at the lowest frequency range. The EIS spectra in Figure 2 can be divided into two zones; high and low-frequency regions associated with the dynamics charge and mass transfer resistances [56]. At the highest frequencies, the x-axis intercept of the impedance arc on the real axis is called high-frequency resistance which is the summation of the ionic resistance of the membrane and electric resistances of fuel cell components such as GDLs and bipolar plates. The semicircle on the left-hand side of the Nyquist plot is called a high-frequency arc correlated to the hydrogen oxidation reaction, and the anther arc presents a mass transfer behavior [57]. If an FCEV accelerates, the fast kinetics of electrochemical reactions in PEMFCs is required. The different reaction rates involve charge transfer reactions hydrogen oxidation and oxygen reduction, as well as the time constant of these reactions. The Nyquist plot of the stack generating 20 A of current indicates the largest high-frequency arc since the reaction and the charge transfer rates were slowest. The Nyquist plot of the stack generating 130 A of current indicated that the highest reaction kinetic rate was provided if it is compared to other current levels. The high-frequency arc of 130 A seems to be the smallest since the fast kinetics and proton-transfer rate at the anode results in a smaller capacity element compared to the other arcs. According to the semicircle at low-frequency, the arc from generating current 20 A (high voltage compare with other arcs) provided the largest area that is distinguishable from the other arc areas. It may be due to higher humidity in the system. As known that the redox reaction in PEMFC is exothermic, so the higher current generation leads to lower humidity. Another interesting point of view is about an increase in sizes of the arcs at low-frequency compared to the high-frequency arcs. Most cases in Figure 2 except at 20 A have the bigger loops at the low-frequency range due to the increased mass transfer limitation [58]. Many earlier studies have found similar outcomes [59-61]. It can be described that the kinetic rate of an electrochemical reaction on the catalyst surfaces was fast, but the mass transfer rate was inadequate to provide sufficient reactants to the catalyst surfaces. In other words, the reactants reaching the catalyst surfaces are consumed immediately, however; the system cannot provide sufficient reactants to continue driving the electrochemical reaction on the electrode surfaces. The obtained results in this part of the work provide an initial understanding of significant mass transport issues, therefore; diffusion processes when PEMFCs are operated with load variation should be significantly observed. The load or speed differentiation in the driving cycle would bring about catalyst and membrane degradation as mentioned in Table 1.

3.2 Hysteresis Loops of I-V Curves Observed during Reference Profile Operation

As mentioned in load profile creation, the hysteresis of polarization curves or I-V curves can be observed during the repetitive increase (from 0 A to 130 A) and decrease (from 130 A to 0 A) in generating current. The upper curves of hysteresis loops were measured as the generated current increases, and the lower curves were measured as the generated current decreases. To verify the consistency of PEMFC stack performance at the end of each stage of the reference profile the areas of the hysteresis loops were monitored. It was found that as the profile progresses, the area of the hysteresis loops enlarged as shown in Figure 3. This phenomenon feasibly corresponded to the drying and flooding situations in the PEMFC stack. If flooding happens on the cathode side and then operating the PEMFC stack at a higher current can make worse voltage loss due to additional water is produced [62]. Notable information an obtained hysteresis loop after load cycling possesses a slightly larger area than the one obtained after start-stop cycling. The voltage degradation rates calculated from I-V curves created as the generated current decreases were 0.31 mV h^{-1} for load cycling and 0.28 mV h^{-1} for start-stop cycling. It can be assumed that stack voltage could be recovered, however; such results cannot guarantee the recovery process in long operating duration. It is known that there are three main types of losses; activation loss, ohmic loss, and concentration loss can be investigated *via* an I-V curve from low current density to high current density. Figure 3 illustrates that the highest voltage losses of the test performance were related both to the activation and ohmic losses, suggesting that the fuel cell components are degraded.

This is an interesting issue for further study to analyze the degradation mechanism of materials. A driving behavior includes load cycling and start-stop cycling leads to oxidation/reduction cycling principally leads to corrosion of carbon support, catalyst dissolution, or membrane delamination [63], explaining the electrochemically reactive surface area reduction and then the activation losses' growth. While the cause of the ohmic loss relates to the resistance to the flow of electrons through the electrically conductive PEMFC components and to the flow of ions through the membrane [64]. Previous publications suggested the solution of these issues, for example, modifying a catalyst surface structure, controlling relative humidity around 40%, or designing a water management system [65-66]. Since the voltage profile of each cell was monitored, it was possible that the degradation of a single cell constructed in the stack would lead to stack voltage degradation. When the stack was run under either load cycling or start-stop cycling conditions, the findings showed that all cells in the stack delivered the same voltage level, as illustrated in Figure 4. According to Table 1, driving behaviors primarily result in heat accumulation and temperature cycling, both of which significantly influence FC material deterioration. As a result, heat accumulation and temperature cycling were detected during the stress test, as shown in Figure 5. The temperature profiles of the PEMFC stack are shown in Figure 5, which were obtained from two test profiles: load cycling and start-stop cycling. The temperature profile can be divided into three categories in the case of load cycling: (i) high frequency and high peak-to-peak amplitude, (ii) high frequency and low peak-to-peak amplitude, and (iii) low frequency and high peak-to-peak amplitude. The operating temperature was set at 55^{o}C, however, the actual average temperatures when the current was pulled at 100, 70, and 20 A were 56.5, 54.6, and 51.3^{o}C, respectively. In the initial period (from 0-150 h), the results indicated a high frequency of the temperature cycle which was 0.65 round h^{-1}, while peak-to-peak amplitude was 8^{o}C. At the beginning of the stack operation temperature was raised to achieve the set temperature. Drawing the current as a cycling process led to heat accumulation, so the peak-to-peak amplitude was decreased in the period of 120-150 h. A high frequency (0.51 round h^{-1}) and a low peak-to-peak amplitude (2^{o}C) were found in the middle zone to stabilized operating temperature close to 55^{o}C. In the duration of 251-605 h, low frequency and high peak-to-peak amplitude with 0.15 round h^{-1} of frequency and 8^{o}C of peak-to-peak amplitude were observed, and this situation related to stack recovery that will be discussed in detail in the next section. The heat accumulation was detected again at the end of load cycling after the recovery effect had faded. Because the relative humidity of the system was kept constant at 1.8, the effect of relative humidity is not stated. As shown in Figure 6, the heat accumulation phenomena is linked to chemical degradation that produces radicals and peroxide assault on Nafion (membrane dehydration). The process causes permanent degradations such as membrane thinning and pinhole development, which have an impact on the membrane's mechanical strength and the increase in gas crossover [67]. According to the start-stop situation, insufficient input gas supply raises real system temperature, whereas insufficient input gas supply raises potential pressure in the anode [68]. The average temperature at start-up condition was 56.0^{o}C, whereas the on at stop condition was 36.0^{o}C. At stop conditions, the average system temperature was the lowest because the supplied reactants were cut off leading to the system was cooled down. The relative humidity was cut off was also cut off resulting in 0 of the relative humidity, but the relative humidity at the start-up condition was 2.2 that was an overshooting value compared to the setting relative humidity. It is due to the redox reaction was driven to achieve a setting generated power. The reaction kinetics variation created a more exothermic reaction, then the temperature inside the stack was significantly enhanced. This discussion is supported by the different temperatures of outlet-and inlet- reactants (ΔT) illustrated in Table 5. The ΔT observed under the start-stop condition was significantly higher than the ΔT reported from the load cycling condition. It is noteworthy that the average peak to peak amplitude of temperature was 19^{o}C which is meaningfully higher than the one that happened in the load cycling condition. It implies that the system temperature and humidity were dramatically changed [69] that possibly impinges on a decrease in the initial elastic modulus and the yield stress, a paltry decrease in the post-yield tangent modulus of membrane and an increase in the yield strain [70]. In this work, the start-stop cycles had been operated for 600 h, thus; temperature cycling and humidity cycling were created. It has a high possibility to generate mechanical degradation of the membrane such as perforations, cracks, tears, and pinholes [71]. As a result, the load cycling in the reference stress test profile seems to have a stronger effect on voltage and materials degradations than the effect of start-stop cycling conditions. This thought is supported by voltage degradation rates determined from our experimental work; the voltage degradation rate found from load cycling condition was 0.61 mV h^{-1} and the rate generated by start-stop cycling was 0.42 mV h^{-1}. The discussion about voltage degradation will be presented in detail in sections 3.3 and 3.4.

3.3 Effects of Test Cycle Repetitions on Voltage Degradations

The inclination of the voltage degradation concerning the hours of operations is reported in Figure 7. The tendency of voltage changes was monitored at the generated current of 20 A, 70 A, 100 A and 130 A selected from the minimum current value, to the current value corresponding to the average, the nominal and the maximum power conditions, respectively. The voltage values were obtained from I-V curves of stack polarization behavior diagnosis that was scheduled for every 24 h. The reference test results are particularly presented with the dashed lines, while the dotted line represents the new measurements obtained under the accelerated stress test (Hf). Note that the accelerated stress test provided 50 cycles (repetitions) of load cycling and start-stop cycling, whereas the stress test proceeded 10 cycles of them. The same procedures of the reference test campaign for the pre-conditioning, the warm-up and the stationary conditioning steps were repeated to compare the experimental results. In the case of the accelerated stress test profile, the end of test conditions was attained after only 3 days of start/stop cycling. By comparison with results from the stress test, the stack voltage changes during the accelerated stress test indicated a similar behavior in voltage degradations from the pre-conditioning step to the end of the load cycling step. This behavior was because FC ageing seems to be not accelerated by the number of repetitions. However, significant results appeared after the stationary conditioning step, after the load cycling process. In the scenario of accelerated stress test (high frequency (Hf) cycles) all the voltage drops were irreversible in opposition to the behavior of the stack during the stress test. The results from the stress test exhibited an important voltage recovery during the stationary conditioning step. To assert this explanation hysteresis loops of I-V curves before and after the stationary conditioning step (second conditioning in Figure 7) were observed. Results from Figure 8 show that the PEMFC stack, operated with the stress test, revealed a recovery process after the stack was stationary conditioned. On the contrary, the hysteresis curve obtained with the accelerated stress test (afterload cycling and stationary conditioning) was in the middle of the hysteresis curves measured during the stress test (before and after conditioning). An overview of the voltage degradation involved the durability of the PEMFC stack. The stress test required 794 h (33 days) to finish the process, while the PEMFC stack can be operated with the accelerated stress test for only 456 h (19 days) to achieve the same voltage degradations. The results also stated 42% of operating time reduction. Additionally, the polarization behavior of stacks analyzed after finishing both tests presents the effect of the number of cycle repetitions as seen *via* the superposition of the curves (Figure 9). It can be concluded that increasing the number of cycle repetitions in the *ad-hoc* accelerated stress test procedures can be considered as an accelerating stress factor, nevertheless; in particular, it has to be increased proportionally with the real load dynamics (frequency of the reference load cycling). It can be observed that only two days of accelerated start-stop cycles were sufficient to generate the same level of voltage degradation obtained after fifteen days of start-stop cycles in the reference profile. Since the impacts of recovering on stack degradation are important investigations, the results from conditioning tests will be discussed in section 3.4. Table 6 makes a comparison between the voltage degradation rate of PEMFC stacks operated under the stress test and accelerated stress test profiles. There are two interesting parameters; repetitions and types of cycling, impacting the voltage degradation rates of PEMFC stacks. The accelerated stress test manipulated with 50 repetitions per day led to higher degradation rates either in load cycling or start-stop cycling step. An accelerated factor of the start-stop cycle was dramatically higher than the factor of load cycling. The voltage degradation rate of PEMFC is typically acceptable in the range of 0.0003-0.5 mV h^{-1} [5], thus; an increasing number of test cycles per day is a promising tool for fuel cell lifespan determination. In terms of materials degradation, an accelerated circumstance theoretically results in Pt dissociation/agglomeration and re-deposition phenomena leading to an electrochemically active area reduction [72]. As a consequence, also at a proper stop and air feed conditions, the cathode potential variation is not sufficient to inverse the Pt oxidation [73], as supposed for the reference stress test voltage recovering. The drastic degradation generated by start-stop cycling is relevant to severer conditions such as high temperature, low humidity, fuel and air starvation, etc. [74-75].

3.4 The Relation between Energy Generation and Voltage Loss during the Stress Tests

Figure 10 displays the voltage loss in the energy domain, and as observable, during the accelerated test only 208 kWh was produced instead of the 250 kWh required in the stress test; resulting in about 17% of the decrease in energy generation. During the start-stop stage, only 2 days were sufficient in case of accelerated start-stop repetition to attend the voltage degradation value corresponding to the end of the stress test (blue square in Figure 10). As consequence, the test was stopped, and an average degradation rate of 8.00 mV kWh^{-1} instead of 0.70 mV kWh^{-1} can be stated for the accelerated and the reference stress tests, respectively as illustrated in Table 7. The start-stop process brings about severe circumstances in the cell such as high temperature, rapid voltage cycling, and low humidity those are negative effects on membrane and catalyst decay. Thus, these phenomena can produce irreversible degradation as happened in the start-stop of an accelerated stress test. In terms of the reference stress test, the start-stop region displayed a higher voltage and generated energy. The voltage values after each shutdown are hypothetically higher than before the shutdown since the voltage losses occurring during each sequence current density can be at least partially recovered [76]. The overall voltage losses can be divided into a partially recoverable performance loss taking place under continuous process and a permanent performance loss [77]. To confirm the hypothesis about recoverable performance, the stationary conditionings after the beginning of life, load cycling, and start-stop cycling were observed (Figure 11). The results found that after the start-stop cycling the PEMFC stack generated 2% higher energy (13.360 kWh) than the energy generation after load cycling (13.107 kWh). These results can support the opinion about reversible voltage degradation. The rational reasons for describing the voltage recovery of PEMFC performance can be raised as follows. Accumulated water in electrodes partially blocked reactant transport to catalyst surfaces, and an increased concentration over-potential reduces PEMFC performance. Dry nitrogen gas is normally required to flush water, so the recovery can exist after flushing. In case of membrane damages such as pinhole or micro-cracks caused by severe circumstance in the stack, and these damages leads to reactant crossover. Water product probably seals the membrane defects, and the voltage recovery can be found [78]. In case of high temperature and drying conditions induced with start-stop cycling, membrane shrinking can occur. If the stack humidity is increased by a stop cycle, a decrease in the mechanical stress will be applied to the membrane. Therefore, it is feasible to acquire the recovery process [79]. There are more strategies of recovery phenomenon such as platinum oxide reduction by decreasing a cathode potential or the decrease of the cathodic potential during shutdown to eliminate contaminants from ionomers [80-81]. They are significant issues that should gain attention from researchers. The stack voltage degradation as a function of generated energy determined *via* accelerated stress test was slightly higher than the degradation found from the stress test (orange square in Figure 10). Even the average voltage degradation rate (1.98 mV kWh^{-1}) at the load cycling stage of the accelerated stress test was approximate to the value (1.87 mV kWh^{-1}) of the stress test, the accelerated factor (11.40 mV kWh^{-1}) of the stack operated under the accelerated stress test was higher than the value (1.06 mV kWh^{-1}) created by the stress test. It is worth noting that the accelerated profile is appropriate to investigate irreversible voltage losses.

4 Conclusions

This work starts with an overview of the effects of load variations and start-stop conditions, mainly induced by common driven cycles. Particularly, load variations and start-stop repetitions resulted in the most recurrent stress factors in FC ageing for automotive applications. To reduce both time and costs of experimental activities aimed at degradation analysis and lifetime prediction, the accelerated stress tests are introduced. The objective is to validate an *ad-hoc* accelerated stress test procedure directly based on the real application power demand, to study the PEMFC stack ageing in a more consistent as possible condition concerning the real application. Starting from a real load profile, suited load sub-cycles can be obtained. These sub-cycles are obtained from the real load profile, separating the load variations dynamics from the start and stop occurrence. To this purpose, the same produced energy must be kept in both the reference and accelerated profiles. Moreover, the load cycling amplitude must be limited between the minimum and maximum most recurrent values of the real load profile while overload and start-stop conditions must be considered as a separated sub-cycle. Once the reference sub-cycles are obtained for the real load dynamics, the accelerated profile can be obtained directly increasing the number of the sub-cycle repetitions. The authors demonstrate a consistent voltage degradation between the results obtained under the accelerated and reference tests. The better comprehension of the relation between speed variation in the stress test profile and the possibility of stack performance decay was obtained from preliminary investigation *via* EIS at the beginning of stack life. When the PEMFC stack is accelerated by higher loading demand, the fast kinetics of electrochemical reactions in PEMFCs is desired. Thus, the severe operating conditions such as low humidity and mass transport problem may be generated. These conditions lead to catalyst and membrane degradation resulting in the reduction of the PEMFC stack performance. The diagnostic results from the hysteresis loops of I-V curves measured during reference profile operation indicate stack voltage recovery, when voltage degradation rates obtained from load cycling was 0.13 mV h^{-1} and 0.28 mV h^{-1} for start-stop cycling. The system temperature and humidity were dramatically changed during load cycling and start-stop conditions. The different temperature detected under the start-stop condition was significantly higher than the different temperature conveyed from the load cycling condition. The average peak to peak amplitude of temperature was 19^{o}C which was higher than the one that occurred in the load cycling condition. According to test cycle repetitions, it is observed that increasing of 5 times the number of cycles' repetitions leads to a factor of about 1.8 can be obtained in voltage degradation for load cycling both in time and in 1.06 energy domain, while an accelerated factor of 5.7 and 11.40 are observed for start-stop cycling in time and energy domain, respectively. The reduction of both time and costs (in terms of consumption) are evaluated. The test campaigns show a time reduction of about 42% with a decrease in consumption by about 17%. The opinion about reversible voltage degradation can be supported by energy generated during the stress test. The results stated that after the start-stop cycling the PEMFC stack generated higher energy (13.360 kWh) than the energy generation after load cycling (13.107 kWh). To conclude general indications of the procedure development of *ad-hoc* accelerated stress tests particularly for automotive applications can be deduced. Starting from a generic dynamic load profile (real load profile), it is possible to obtain ad-hoc accelerated stress test procedures if suited load sub-cycles can be obtained. These sub-cycles will be obtained from the real load profile, separating the load variations dynamics from the start and stop occurrence. (i) the same produced energy must be conserved, (ii) the load cycling amplitude must be consistent with the real load current density distribution (the sub-cycle has to cycle between the minimum and maximum most recurrent values of the real load profile), (iii) in case of overload conditions, these have to be treated with a separated sub-cycle, (iv) the occurrence of which must be defined based on the frequency of the real overload occurrence, (v) start-stop repetitions must be considered as a separated sub-cycle, (vi) once the reference sub-cycles are obtained for the real load dynamics, the accelerated profile can be obtained directly acting on the load cycling frequency (increasing the number of the sub-cycles repetitions). Futures works will be dedicated to the testing of the impact of the temperature growth in ageing acceleration. This study will aim to assess both the load cycling frequency growth, the start-stop repetitions and the temperature growth as the major stress factor for accelerated stress test development and ageing prediction.

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Figure Captions

Figure 1: Structures of (A) reference profile and (B) accelerated profile

Figure 2: Nyquist plots observed at different DC currents

Figure 3: Hysteresis loops of I-V curves

Figure 4: The voltage profiles of each cell in PEMFC stack (A) load cycling condition and (B) start-stop condition

Figure 5: The temperature profile monitored during the stress test

Figure 6: Radicals and peroxide attack on membrane

Figure 7: Voltage degradation results of a stress test and accelerated stress test

Figure 8: Hysteresis loops of I-V curves measured from the stress test and accelerated stress test after load cycling

Figure 9: Hysteresis loops of I-V curves measured from the stress test and accelerated stress test at the end of the test

Figure 10: Relation between voltage degradation and generated current obtained from stress test and accelerated stress test

Figure 11: Conditioning results for studying the different main profiles (A) after BoT (B) afterload cycling and (C) after start-stop cycling

Tables with Captions

Table 1 The relationship between load behaviors, operating conditions, and materials degradation of PEMFC [6-9]

Driving behaviors	Actual system conditions	Materials degradation
Stationary application		
Long time using	(i) High humidity	*Membrane* cracks, pinholes, peroxide and hydrogen peroxide production *Catalyst* Ostwald ripening and sintering of particles *GDL and BP* corrosion
Automotive applications		
Load cycling	(i) Voltage cycling (ii) Temperature cycling (iii) Humidity cycling	*Membrane* cracks, pinholes, peroxide and hydrogen peroxide production *Catalyst* Ostwald ripening of particles, sintering of particles *GDL and BP* corrosion
Start-stop cycling	(i) High voltage (ii) High temperature (iii) Low humidity	*Membrane* perforations, cracks, tears, pinholes, peroxide and hydrogen peroxide production, hydrogen and air crossover *Catalyst* detachment of catalyst particles from carbon support, Ostwald ripening of particles, sintering of particles, and dissolution of the catalyst *GDL and BP* corrosion
Overload condition	(i) High voltage (ii) High temperature (iii) Low humidity	
Full power	(i) High voltage (ii) High temperature (iii) Low humidity	
Cold starting	(i) Low temperature (ii) High humidity	*Membrane* cracks, pinholes *Catalyst, GDL and BP* corrosion

Table 2 12-cell PEMFC specifications

Specifications	Values
Active area	200 cm^2
Width × height × length (overall dimensions)	246.0 mm × 136.0 mm × 77.5 mm
Operating pressure of H_2	400-700 $mbar_g$
Operating pressure of air	700 $mbar_g$
Temperature range during operation	3-65^{o}C
Range of voltage out	4 to 14 V
Maximum current	130 A
Maximum continuous performance	1 kW
Efficiency	>52%
Coolant	DI-Water

Table 3 Operating conditions

Technical specifications	Range
Hydrogen flow rate	According to the operating current
Airflow rate	According to the operating current
Inlet hydrogen temperature	40^{o}C to validated value
Inlet air temperature	40^{o}C to validated value
Hydrogen pressure	Ambient or 0.4 bar_g
Air pressure	Ambient or 0.6 bar_g
Autogenous air pressure loss	Depending on load current Limitation at 175 $mbar_g$ for 130 A
Inlet hydrogen/air humidity	Dry gas
Cooling temperature	55^{o}C as a limitation
EIS measurement conditions	
Frequency	1000 – 0.1 Hz
Excitation current peak-to-peak	2000 mA
Maximum current of load supplying	200 A

Table 4 The corresponding time and profiles duration

Stage number	Load profile stage	Imposed current	Corresponding time (min)	Repetition per day	Total duration (min)
Reference profile					
2,5,8	Stationary state (Conditioning)	(i) Constant current at 70 A	1,440	1	1,440
3	Cyclic load	(i) Initial current at 20 A	70	10	21,000
		(ii) Medium current at 70 A	20		(15 days)
		(iii) Maximum current at 100 A	50		
6	Start-stop	(i) Stop at 0 A	75	10	21,000
		(ii) Start at 70 A	65		(15 days)
Accelerated stress cycle profile					
2,5,8	Stationary state (Conditioning)	(i) Constant current at 70 A	1,440	1	1,440
3	Cyclic load	(i) Initial current at 20 A	14	50	21,000
		(ii) Medium current at 70 A	4		(15 days)
		(iii) Maximum current at 100 A	10		
6	Start-stop	(i) Stop at 0 A	15	50	21,000
		(ii) Start at 70 A	13		(15 days)

*Stage number shown in the table is related to Figure 1.

Table 5 Recorded ΔT during the load cycling and start-stop cycling conditions

Reactants	Load cycling condition			Start-stop condition		
	T_{inlet} / ºC	T_{outlet} / ºC	ΔT_{avg} / ºC	T_{inlet} / ºC	T_{outlet} / ºC	ΔT_{avg} / ºC
Hydrogen	23.97	35.59	11.62	23.52	41.59	18.07
Air	22.72	46.74	24.02	23.40	50.64	27.24

Table 6 Average voltage degradation rates of PEMFC stacks

	mV h^{-1}		
	10 repetitions per day	50 repetitions per day	Resulting accelerated factor
Load cycling	0.61	1.10	1.80
Start-stop cycling	0.42	2.40	5.70

Table 7 Average voltage degradation rate in terms of the relation between voltage and generated energy

	mV kWh^{-1}		
	10 repetitions per day	50 repetitions per day	Resulting accelerated factor
Load cycling	1.87	1.98	1.06
Start-stop cycling	0.70	8.00	11.40