Degradation Mechanisms in Automotive Fuel Cell Systems

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Degradation mechanisms in automotive PEM fuel cell systems are categorized, in this deliverable, in regard to the degradation mechanisms of each component of PEM fuel cell stack, namely: membrane, catalyst layers, gas diffusion layers, bipolar plates and sealing gaskets. The underlying degradation mechanisms of each of the aforementioned structural component of the cell are decomposed with brief explanation of the physical phenomena causing the degradation and the inter-relation of the influence of one constituent of the structural component on the other. The analysis based on available data from the project partners and literature survey leads to the conclusion that the main degradation mechanisms of the cell depend on high number of different variables, such as MEA manufacturing process, assembly, operating conditions, thermal cycling, relative humidity cycling, subfreezing ambient temperature, load cycling, etc. Therefore, the main degradation mechanisms have to be determined based on the particular and highly detailed cell configuration. The mitigation strategies are proposed for each structural component, although some of the requirements may be in confrontation with each other. PEM fuel cell degradation cannot be completely suppressed, however by closely monitoring the cell operation and adapting the operating conditions to the particular cell design, they can be significantly minimized. The accelerated stress tests are surveyed and listed for each structural component, and some of them are compared vs. real-time investigation under certain operating conditions (e.g. carbon corrosion) with good agreement. General conclusion is that the ability of
the accelerated stress tests to predict the real-time operating conditions inside
the cell is of a limited reliability, due to the nature of simulating only a limited
number of degradation mechanisms at the same time, with quite limited
influence on other structural components of the cell, unlike the real-time field
testing. However, by monitoring and understanding each of the underlying
degradation phenomena and modifying the cell design and operating conditions,
the remaining useful lifetime of the cell can be significantly prolonged, even
under highly transient operating conditions. The analysis and evaluation of the
mechanical, chemical and thermal factors contributing to ageing and/or early
failure of the balance-of-plant components, particularly the air compressor and
the humidifier, identified the most critical ageing factors for the conditions of
the intended use, i.e., inside the range extender trailer, and identified those that
will need to be characterised in laboratory experiments.

Revision History

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1. Introduction

One of the goals of Giantleap’s WP1 is to improve understanding of degradation phenomena in fuel cell stacks and Balance of Plant (BoP) components. Based on the available data from the project partners and literature survey this report categorises and describes degradation mechanisms for each of the stack components, namely: membrane, catalyst layers, gas diffusion layers, bipolar plates and sealing gaskets. The underlying degradation mechanisms of each of the component are decomposed with brief explanation of the physical phenomena causing the degradation. The accelerated stress tests are surveyed and listed for each structural component, and some of them are compared vs. real-time investigation under certain operating conditions. The most relevant degradation mechanisms in fuel cells for automotive systems are identified such as degradation of the catalyst layer caused by carbon corrosion due to frequent starts and stops (air fuel front), loss of catalyst active area caused by platinum dissolution and sintering due to frequent voltage cycling, loss of catalyst active area due to adsorption of contaminants from the inlet gases, mechanical degradation due to thermal and humidity cycling induced by the load profile as well as by the environment in which the vehicle operates.

The report also contains an analysis and evaluation of the mechanical, chemical and thermal factors contributing to ageing and/or early failure of the balance-of-plant components, particularly the air compressor and the humidifier.

2. Polymer electrolyte membrane degradation

The membrane in a PEM fuel cell system is sandwiched between the anode and cathode electrode. The primary functions of the membrane are to conduct the hydrogen protons, support the anode and cathode catalyst, and prevent the oxidizing and reducing agents on the anode and cathode side, respectively. The requirements for highly efficient membrane are high ionic conductivity, reactant gas impermeability, thermal and chemical stability, etc. [1,2]. The commonly used membranes in PEM fuel cells are perfluorosulfonic acid membranes, such as Nafion® (DuPont™), Gore-Select® (Gore™), etc. Although extensive studies have been carried out in regard to the membrane degradation and failure mechanisms in PEM fuel cells, reliability and durability of the membrane is still elusive component of the diagnostics and impedes the commercialization of PEM fuel cells.
2.1. Membrane degradation mechanisms

The membrane degradation can be roughly classified in three categories: mechanical, thermal and chemical/electrochemical [3,4].

2.1.1. Mechanical degradation

Mechanical degradation results in early failure due to cracks, pinholes, perforations and tears of the membrane, often caused by the congenial membrane defects or improver fabrication process of the membrane-electrode assembly (MEA). During the assembly of PEM fuel cell, the interfaces between the bipolar plate lands and channels, and the sealing edges are subjected to excessive and non-uniform mechanical stress, are prone to perforations or tears during the assembly of the single cell or a stack. Once assembled, the membrane is also subjected to the relative humidity cycling, resulting in repetitive swelling and shrinkage of the membrane, resulting in detrimental mechanical durability of the membrane [5-10]. The migration of the catalyst on the membrane surface and the seal decomposition reduce the ductility of the membrane and hinder its mechanical strength. The perforations and pinholes result in crossover of the reactants into the reverse electrodes, generating local hot spots, resulting in highly increased membrane degradation due to the highly exothermic combustion reaction between the oxidizing and reducing agents and consequently result in a catastrophic failure.

2.1.2. Thermal degradation

The most favorable working temperatures in PEM fuel cells for achieving high membrane hydration are 60 °C to 80 °C. Conventional membranes are subject to critical breakdown at temperatures exceeding 80 °C due to glass transition of PFSA polymers, additionally, the membrane water content at higher temperatures is decreased due to the decreased relative humidity of the reactants thereby hindering the performance of PEM fuel cell system [11, 12]. The polytetrafluoroethylene (PTFE)-like backbone gives Nafion® membranes increased thermal stability up to temperatures beyond 150 °C, however, at higher temperatures the Nafion® is decomposed [13]. There are a number of papers dealing with thermal stability of Nafion® membranes at higher temperatures [14-17], however, these temperatures are in several hundreds of °C and far exceed the PEM fuel cell operating temperatures therefore they are not relevant for this study.

Another requirement for the membrane is the capability of rapid startup and stable performance in subfreezing temperatures, as well as thermal cycling conditions, especially in the automotive and...
portable applications. Studies carried out on the state of water in PFSA membranes below freezing temperatures suggest that three different states of water exist in the membrane [18]. Besides liquid water and water vapor, the third phase is termed the “free water” or “dissolved water” inside the membrane, which is not intimately bound to the polymer chain, therefore it is subject to freezing in subzero temperature environments. However, it was found that the “free water” is not entirely subject to freezing [19, 20]. The contact resistance of the interface between the membrane and electrodes was found to increase after thermal cycling, even though the membrane’s ionic conductivity was not affected in the process [21]. Another study found that after 385 thermal cycles between temperatures +80 °C and -40 °C, the membrane’s ionic conductivity, gas impermeability and mechanical strength were severely impaired, although without catastrophic failure detection. In order to mitigate the detrimental effect of thermal cycling and detrimental effects caused by freeze/thaw cycles during operation, and the removal of residual water from the system, solution purging and gas purging are proposed during startup and shutdown.

2.1.3. Chemical/electrochemical degradation

The research conducted in regard to the oxidizing and reducing agent crossover to the reverse sides of the membrane has deduced that the process is relatively slow and results in only 1-3% loss in fuel cell operating efficiency [22,23]. However, the highly exothermal combustion of oxidizing and reducing agent can result in pinholes in the membrane, potentially causing a catastrophic failure of the system. The chemical reactions on the anode and cathode catalysts can produce peroxide and hydroperoxide radicals, responsible for the detrimental chemical degradation of the membrane and catalyst layers [24,25]. The generation of the aforementioned radicals is especially pronounced at the open-circuit voltage (OCV) and low humidity operating conditions. Several studies propose the explanation on the origin of the radical formation inside an operating cell, from the anode or the cathode side, but with conflicting results, while some studies have observed no noticeable difference between the anode and cathode side [26-31].

The occurrence of foreign cations inside PEM fuel cell can significantly decrease the cell performance by adsorbing on the membrane or the catalysts. The origin of the foreign cations ranges from the corrosion of the structural components of the cell, to impurities in the air stream, humidifiers, etc. [32], and the detrimental effect is caused by higher affinity of the foreign cations to the sulfonic acid group of the PFSA membrane when compared to the hydrogen cations. However, the foreign cationic contamination is usually minor unless the contamination concentration exceeds 50% of sulfonic acid.
groups in the PFSA membrane [33]. The more prominent membrane deterioration due to cation contamination is a result of the altered water transport inside the membrane, which is caused by only 5% contamination, directly affecting the membrane's ionic conductivity, resulting in more severe membrane dehydration [34]. Trace metal cation contamination, originating from the corrosion of metallic bipolar plates such as Fe^{2+} and Cu^{2+}, results in pronounced membrane thinning and performance deterioration due to catalyzing the radical formation reaction [22]. The aforementioned mechanisms lead to membrane thinning and eventual pinhole formation, resulting in catastrophic failure of the cell. The effect is explained as unzipping of the polymer end groups, or scission of the polymer chains [61,62,27], where the measurement of the rate of the fluoride loss has been considered as a prominent method to determine the rate of PFSA membrane degradation [35].

2.2. Membrane degradation mitigation strategies

Special considerations must be applied during the design of the flow field and the MEA structure in order to prevent mechanical failure of the membrane caused by local membrane dry out which is pronounced in the areas in close proximity to the reactant inlets [36-38]. Membranes reinforces with e-PTFE have shown an order of magnitude longer lifetime when compared to the non-reinforced membranes of similar thickness [35,39,40], as shown in Figure 1. Several studies have focused on achieving longer durability at operating temperatures exceeding 100 °C [41-44] by doping the membranes with different compounds, however the focus of this work are operating temperatures below 100 °C. Increased chemical and electrochemical reliability in regard to the peroxide formation is achieved by incorporating the inhibitors and free-radical stabilizers into the membrane structure, or including the sacrificial materials [30, 45-49]. Since the mitigation strategies for the membrane are primarily oriented towards altering the design and fabrication process, the experimental mitigation strategy for increasing the membrane reliability are oriented toward achieving high relative humidity, i.e. membrane water content, along the entire flow field, especially near the reactant inlets.
3. Electro catalyst and catalyst layer degradation

The commonly used electrocatalysts in PEM fuel cells are Pt, and Pt-transition metal alloys, e.g. Pt-Co, Pt-Cr-Ni and Pt-Ru-Ir-Sn, on conductive supports. The conductive supports are high surface area carbon materials, e.g. Vulcan-XC® 72, Black pearls® BP2000 and Ketjen black®. Such catalysts meet the performance and cost requirements for high-volume production of PEM fuel cells. Although commonly used, such materials have unsatisfactory performance under dynamic operating conditions, high relative humidity, elevated temperature, low pH values and the oxidizing and reducing environments [32]. Membrane degradation mitigation strategies

3.1. Electro catalyst and catalyst layer degradation mechanisms

Numbers of studies are devoted to the investigation of the catalyst layer degradation mechanisms during long term operation. The Pt catalyst can be contaminated by impurities from the reactants' supply system [23], the electrochemically active surface area (ECSA) can be reduced by sintering or migration of the Pt particles on the carbon support during operation, the Pt particles can also be detached from the carbon support and dissolved in the ionomer phase, and finally the carbon

\[\text{Figure 1. Comparison of Gore reinforced membranes and non-reinforced membranes. (a) Lifetime of various membranes in accelerated fuel cell conditions; (b) H}_2\text{ crossover rate as a function of time.}\ [1]\]
support is prone to degradation, termed carbon corrosion. The sintering and coarsening of the Pt particles during operation are explained by several mechanisms. The mechanism of dissolution of small Pt particles and deposition on larger particles, causing the particle growth, is termed the Ostwald ripening [50]. Besides Ostwald ripening, another mechanism related to the Pt particle dissolution in the ionomer phase can cause precipitation of Pt in the ionomer membrane, as a result of the Pt ion reduction, and when combined with the hydrogen crossover from the anode side, results in significant reduction of the durability and reliability of the membrane, as well as reduction in membranes' ionic conductivity [51]. The Pt particle agglomeration on the carbon support can occur on the nano-scale or the atomic scale. The nano-scale agglomeration is a result of random cluster collisions and results in log-normal distribution of the Pt particle size, with peak in smaller particle sizes, and tail in larger particle sizes. The atomic-scale agglomeration results in the opposite log-normal distribution of the Pt particle sizes when compared to the nano-scale agglomeration [52]. It is still unknown which of the described mechanisms is dominant in regard to the localized Pt particle growth [53], but it is evident that the result is the decreased ECSA of the cell [54]. Another detrimental mechanism leading to Pt particle growth and reduction of the ECSA is a result of the metal oxide layer formation on the anode and the cathode side during operation [55, 56].

Carbon support corrosion of the catalyst layers has gained momentum in industrial and academic research, evident from a number of different studies [6,57,58]. There are two proposed driving mechanisms of carbon corrosion relating to the operation mode in PEM fuel cell stacks. The first is induced by the transition between the startup and shutdown cycles and the second one is induced by the localized fuel starvation on the anode side of the cell under steady state operating conditions. The first one is termed the air-fuel front, it is caused by non-uniform distribution of the hydrogen along the anode side of the cell in combination with the oxygen crossover from the cathode side of the cell, it most likely occurs during the startup and shutdown of the cell. The fuel starvation is caused by different mechanisms. It can result from a non-uniform fuel distribution between the neighboring cells in a stack during high utilization intervals, by the occurrence of higher accumulation of liquid water inside the cell, or due to the localized blockage of the portions of the active area caused by ice formation under subfreezing ambient temperature operating conditions. The result of starvation, caused by localized hydrogen exhaustion, leads to the negative anode potential resulting in water and carbon oxidation [34].

Carbon corrosion, although thermodynamically unstable, should be normally negligible in PEM fuel cells at potentials lower than 1.1 V vs. reversible hydrogen electrode (RHE) due to slow kinetics.
However, the electrocatalysts consisting of Pt/C or PtRu/C accelerate the carbon corrosion rates by lowering the carbon oxidation potentials up to 0.55 V vs. RHE, or even lower [59]. If there is sufficient amount of water inside the cell, the carbon corrosion is inhibited by the H₂O oxidation process, but it will occur if the water in the membrane is depleted at high current densities not sustainable by the H₂O oxidation process [60]. The cell reversal mechanism, driven by the fuel starvation, has a detrimental effect not only on the catalyst layer durability, but also on the gas-diffusion layer and bipolar plate durability as well. The carbon corrosion results in the decreased conductivity of the electrodes, increased contact resistance and consequently the increased total resistance of the cell, as well as the decreased catalyst support sites resulting in catalyst material sintering and, in extreme cases, a structural collapse of the electrodes [61].

Besides the increased membrane degradation, the water phase transformation, caused by the ice expansion and shrinkage during thawing process, and the swelling and shrinkage of the membrane at subfreezing temperatures and under temperature cycling conditions, respectively, can also affect the catalyst layer performance due to altering of the membrane/catalyst layer interfaces and the catalyst layer internal structure [21,62,63]. Additionally, due to dissolution of the ionomer of PTFE during cell operation, the catalyst layer hydrophobic properties are altered, hindering the performance due to altered water management and mass transport properties of the catalyst layer [64]. From a diagnostics point of view, it is easy to see that the catalyst layer degradation is highly a complex process due to different structural components involved, and outlining each of the constituent mechanisms is quite difficult due to non-uniform nature of the distribution of the operating parameters (i.e. current, temperature, relative humidity, liquid water, etc.) inside an operating cell.

3.2. Mitigation strategies for electrocatalyst and catalyst layer degradation

The electrocatalyst and catalyst layer durability in PEM fuel cells can be increased by choosing the appropriate operating conditions. The Pt dissolution from the carbon support is decreased at lower operating electrode potentials, resulting in increased Pt stability at the anode side when compared to the cathode side. The reduction in ECSA in respect to the operation time can be significantly decreased by operation at low relative humidity and low temperatures [61], as shown in Figure 2., however, the carbon corrosion rates have been found to increase under low relative humidity operating conditions. It was also found that the Pt particle growth rates are significantly greater during standardized experimental accelerated-stress tests with potential cycling, when compared to the steady state operation [65].
The carbon corrosion due to fuel starvation can be minimized by enhancing the water retention on the anode side of the cell, achievable by modifying the PTFE and ionomer by adding water blocking components, as seen in the water electrolyzer analysis in Figure 3. [6]. Alleviation of the detrimental effects of freezing and rapid startup of the cell, and consequently achieve increased durability, can be achieved by employing two strategies during system startup or shutdown under subfreezing ambient temperatures. The first one is termed the “keep-warm” method, it is based on consuming the power from a continuous low power source, such as battery or hydrogen fuel converter, in order to keep the temperature of the PEM fuel cell system above a threshold during the shutdown process (e.g. parking period in automotive applications) [66-68]. The other method is to gradually increase the temperature of the system during startup above the water freezing point, however this method requires a substantial power source in order to produce the required amount of heat and it needs to be combined with a residual water removal strategy (i.e. purging the system or even washing it away.)
with antifreeze solution prior to shutdown [21]) due to the sudden thawing of ice and occurrence of higher quantities of liquid water inside the cell [6,69,70].

Figure 3. Comparison of different anode structures in severe failure testing. Each cell has an equivalent cathode (∼0.7mg cm⁻² Pt, supported on carbon). Testing conducted at 200mg cm⁻², fully humidified nitrogen on anode. Anode loading at ∼0.3mg cm⁻² Pt supported on carbon (varied materials and compositions). [1]

The sintering of the catalyst particles can be decreased by using Pt-transition metal alloys (e.g. Pt-Co, Pt-Cr-Ni) instead of pure Pt catalysts [71,72], however the studies have shown that the Pt-transition metal alloys develop a skin of monolayer Pt after long testing periods, due to the increased dissolution of the non-noble metals in the PEM fuel cell atmosphere, thus counteracting the advantages of such catalysts [73-75]. The Pt dissolution was show to be dramatically decreased by modifying the Pt particles with Au clusters, resulting in almost unchanged ECSA after 30,000 cycles between 0.6 V and 1.1 V [76], due to non-solubility of the Au clusters. There is a number of studies dealing with modifying the catalysts with different methods in order to increase the anchoring of the Pt on the carbon support, or by graphitizing the carbon support [77-81] which have resulted in the increased durability of the catalyst layers in modern commercial PEM fuel cell systems, however, the diagnostics methods and degradation mechanisms are still under development.
4. Gas-diffusion layer degradation

The gas-diffusion layer (GDL) typically consists of two carbon based porous layers, a carbon paper or carbon cloth substrate and a thinner micro-porous layer (MPL) consisted of carbon black powder and a hydrophobic agent. During prolonged operation, the MPL hydrophobicity is reduced as well as during cold start operation [82,83]. There is a limited number of studies on the degradation mechanisms of GDLs, and since the GDL aging procedures are mainly ex situ in order to prevent the confounding effects from the adjacent catalyst layer and bipolar plate, the correlation between the GDL properties and the PEM fuel cell performance is not clearly understood.

4.1. Gas-diffusion layer degradation mechanisms

It is shown that the GDL hydrophobicity decreases with the increase in operating temperature and when air is being used instead of nitrogen [84], and the changes in the hydrophobicity are attributed to the altered MPL structure. The ex situ experiments with submersion of GDL in hydrogen peroxide concluded that the weight of the GDL is reduced with submersion time, and that the contact angle is increased, leading to a conclusion that the carbon oxidation is taking place in the MPL [85], another study concluded that the submersion of the GDL in sulfuric acid leads to a rapid decrease of the contact angle of the GDL [86]. A comprehensive study of different GDL properties over 1500 hour aging time and freeze-thaw cycles has shown that the PTFE and carbon composites inside the GDL are susceptible to chemical and electrochemical degradation, due to peroxide formation and oxidation, respectively [85,87]. Another study has found that the PTFE decomposition in the electrodes results in two times higher performance loss when compared to the Pt catalyst agglomeration after 1000 hour of PEM fuel cell operation [88]. The decrease in the PTFE content of the GDL leads to increased water retention inside the GDL, as seen in Figure 4., increasing the mass transport losses and reducing the PEM fuel cell efficiency, especially at higher currents.
4.1. Mitigation strategies for the gas-diffusion layer degradation

The data on mitigation strategies for the gas-diffusion layers is quite poor. The suggestions are to use the graphitized fibers during GDL preparation in order to improve the oxidative and electro-oxidative stability of the GDL [89], and to increase the PTFE content in order to achieve higher contact angle for improved water management of aged GDLs. The incorporation of the graphitized carbon particles, one study has found a 25% reduction in the degradation at current density of 1.2 A cm$^{-2}$.

5. Bipolar plate degradation

Bipolar plates in PEM fuel cells have three general functions: to separate the fuel, oxidant and coolant; ensure homogeneous reactant and product stream distributions; and to collect the current generated by the electrochemical reaction. To fulfill the requirements, the bipolar plates should ideally be characterized by high electrical conductivity, high corrosion resistance, low gas permeability, low thermal resistance, low cost, sufficiently high mechanical properties, etc. Besides graphite, metals and graphite/carbon composites, as well as polymer-based composites with conductive graphite/carbon fillers are evaluated [90-92]. The graphite and graphite composite materials are attractive materials for bipolar plates due to high corrosion and chemical resistance, however, their mechanical properties, permeability to hydrogen, higher specific weight and volume, as well as manufacturability are unfavorable when compared to metals. Metals such as Pt, Ta, Nb and Zr have favorable characteristics for PEM fuel cell applications, however the high price of these metals hinders their commercial application capabilities [93]. Commercially available metals such as Al, Ti and Ni have favorable characteristics for PEM fuel cell applications, however the problem with
these metals is the increased contact resistance between the bipolar plate and the GDL due to formation of thin oxide layer. Stainless steel received attention for PEM fuel cell applications due to wide range of alloys available on the market, however, it is prone to corrosion in aggressive acidic and humid environments, therefore prone to increase in the contact resistance [94]. Additionally, the cations produced during the corrosion of stainless steel inside PEM fuel cell atmosphere leads to increased degradation of the membrane and the catalyst layers due to production of Fe, Ni and Cr ions, as discussed in the previous chapter [90,95].

5.1. Mitigation strategies for bipolar plate degradation

The current work in mitigation strategies for bipolar plates is mostly based on using graphite/polymer composites or prescribing different coatings for metal bipolar plates, e.g. noble metals, nitride or carbide based alloys, etc., to improve the stability of the bipolar plates in PEM fuel cell environments [90,96], under real or simulated operating conditions. The application of the protective coatings on the bipolar plates yields a risk when the bipolar plates are subjected to thermal cycling operating conditions, and increases the risk of inception of micro-pores and micro-cracks during operation due to difference in thermal expansion coefficients between the coating and the bipolar plate materials. Additional problem with coatings is the poor mechanical strength of very thin coatings, prone to fracture under higher loads to ensure gas-tight stack assembly and the resulting non-uniformly distributed force along the active area of the cell [97], and in case of cracking of the coating layer due to difference in the coefficients of thermal expansion or mechanical stress, the metal ions can migrate from the metallic bipolar plate to the ionomer membrane with adverse effect on cell performance due to contamination of the membrane. Effective strategy for minimizing the effect of difference in coefficients of thermal expansion on the cracking of the coating layer is to introduce an intermediate layer with high bonding strength between the bipolar plate and the coating layer. The mechanical properties of the cell can be deteriorated by thermal cycling, non-uniform current and temperature distribution along the active area of the cell. Improved stability of the metallic bipolar plates can be achieved by subjecting the bipolar plates in atmosphere of acidic electrolyte and passing the current through the bipolar plate material, resulting in improved corrosion resistance without the requirement for coatings, thereby completely avoiding delamination which is the main problem with coatings [98,99], Table 1. shows research on composite bipolar plate materials, with their advantages and disadvantages. Recent research in regard to the development of carbon-polymer bipolar plates has failed to develop stable bipolar plate materials due to the requirement for high carbon loading to achieve sufficient electrical conductivity and the fact that the
resins used in the process are prone to increased degradation rates, resulting in release of the heavy-metal atoms which diffuse and contaminate the membrane, decreasing the efficiency of the cell [100].

Table 1. Practicable coated metallic bipolar plates proposed in the literature, modified from [1].

<table>
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<tr>
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<th>Coating method</th>
<th>Coating materials</th>
<th>Applicable base plate materials</th>
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<td>Au over Ni over Cu</td>
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<td>[101,102]</td>
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<td>DC magnetron sputtering</td>
<td>Ta</td>
<td>X</td>
<td>SS316</td>
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<td></td>
<td>Electroplating</td>
<td>Au</td>
<td>X</td>
<td>SS</td>
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<tr>
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<td>X</td>
<td>X</td>
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<td>Ti-Al-nitride layer</td>
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<td>Sublayer n-type SiC, topcoat Au</td>
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<td>Painting or pressing</td>
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<td></td>
<td>PVD and chemical anodization/oxidation overcoating</td>
<td>Sublayer Ti over Ti-Al-nitride, overcoat transient metal sublayer of Cr(Ti, Ni, Fe, Co) followed by S/Cr acid, or topcoat graphite</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Conductive polymer</td>
<td>NS</td>
<td>Organic self-assembled monopolymers</td>
<td>NS</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Conductive polymers</td>
<td>NS</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coating comprised of carbon fibers contained within a polymer matrix</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Electrodeposition</td>
<td>Conductive polymers polyaniline (PANI) and polypyrrole (PPY)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Multilayer coating (Ni, Au) conductive polymer (polyaniline)</td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>
6. Sealing gasket degradation

The sealing gaskets are placed between the neighboring bipolar plates. The primary functions of the sealing gaskets are prevention of gas and coolant leakage and crossover. Typical sealing gasket materials used for PEM fuel cells are silicone, fluorine caoutchouc and EPDM. Number of studies have been devoted to determining the degradation of different gasket materials in simulated fuel cell environments, as well as in the PEM fuel cell stacks during long-term operation. The traces of the silicone gaskets were observed in the anode and cathode catalyst layers, while the direction of the trace propagation was from the anode to the cathode side of the cell due to the influence of electrical field and the obstruction of the trace propagation by the polymer electrolyte membrane, however some authors have detected the traces of the sealing material decomposition on both sides of the membrane and in the electrodes. The sealing material is also subjected to chemical alteration of the composition due to the combination of the acid environment of the polymer electrolyte membrane, thermal cycling and hydrogen embrittlement. The degradation of the sealing material results in the hindered capability of preventing gas and coolant leakage and crossover, reduced compression force, and it can potentially result in short circuiting of the adjacent bipolar plates. The migration of the sealing material and accumulation on the electrodes results in lower hydrophobicity of the electrodes and potentially induces Pt catalyst poisoning. The sealing material can also migrate to the polymer electrolyte membrane, altering the structure of the membrane and reducing the conductivity and structural mechanical integrity of the membrane, resulting in decreased life time of the cell. Generally, the sealing material must be selected according to the mechanical and chemical properties of the surrounding materials, however, the mitigation strategies for the gasket materials are yet to be determined.
major failure modes of different PEM fuel cell components – summary

The different failure modes and causes are outlined and summarized for each PEM fuel cell structural component in Table 2 and graphically represented in Figure 5.

Table 2. Major failure modes of different components in PEM fuel cells. [1]

<table>
<thead>
<tr>
<th>Component</th>
<th>Failure modes</th>
<th>Causes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>Mechanical degradation</td>
<td>Mechanical stress due to non-uniform pressure, inadequate humidification or penetration of the catalyst and seal material traces</td>
</tr>
<tr>
<td></td>
<td>Thermal degradation</td>
<td>Thermal stress, thermal cycles</td>
</tr>
<tr>
<td></td>
<td>Chemical/electrochemical</td>
<td>Contamination, radical attack</td>
</tr>
<tr>
<td>Catalyst/catalyst layer</td>
<td>Loss of activation</td>
<td>Sintering of dealloying of electrocatalyst</td>
</tr>
<tr>
<td></td>
<td>Conductivity loss</td>
<td>Corrosion of electrocatalyst support</td>
</tr>
<tr>
<td></td>
<td>Decrease in mass transport rate of reactants</td>
<td>Mechanical stress</td>
</tr>
<tr>
<td></td>
<td>Loss of reformate tolerance</td>
<td>Contamination</td>
</tr>
<tr>
<td></td>
<td>Decrease in water management ability</td>
<td>Change in hydrophobicity of materials due to Nafion or PTFE dissolution</td>
</tr>
<tr>
<td>GDL</td>
<td>Decrease in mass transport</td>
<td>Degradation of backing material</td>
</tr>
<tr>
<td></td>
<td>Decrease in water management ability</td>
<td>Mechanical stress, change in the hydrophobicity of materials</td>
</tr>
<tr>
<td>Bipolar plate</td>
<td>Conductivity loss</td>
<td>Corrosion, oxidation</td>
</tr>
<tr>
<td></td>
<td>Fracture/deformation</td>
<td>Corrosion, oxidation</td>
</tr>
<tr>
<td>Sealing gasket</td>
<td>Mechanical failure</td>
<td>Corrosion, mechanical stress</td>
</tr>
</tbody>
</table>
8. An overview of accelerated stress tests

This chapter is dedicated to overview on different ASTs used in the literature with comparison of the AST data vs. FCTT drive cycle, relevant for automotive applications. The emphasis is on the degradation of the catalyst layer and the membrane. The influencing parameters on the catalyst layer and membrane degradation and the corresponding cycling tests are shown in Figure 6.
Figure 6. Influencing parameters and cycling tests for catalyst layer (above) and membrane (below) degradation [132].

The summary for commonly used ASTs for degradation of PEM fuel cell structural components is shown in Table 3.

Table 3. General AST methods in PEM fuel cell lifetime analysis, modified from [1].

<table>
<thead>
<tr>
<th>Component</th>
<th>General criteria</th>
<th>Failure modes</th>
<th>Available protocols</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane/MEA</td>
<td>OCV at reduced RH for chemical stability, RH cycling for mechanical degradation</td>
<td>Chemical stability</td>
<td>Fenton’s test: 30% H₂O₂, 20 ppm Fe²⁺, 85 °C, 3 cycles with fresh reagent</td>
<td>[133]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chemical/electrochemical stability</td>
<td>OCV, 90 °C, with partially humidified H₂ and O₂ (both 30% RH)</td>
<td>[10, 133]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>OCV, 80 °C, with dry air and fully humidified H₂</td>
<td>[10]</td>
</tr>
<tr>
<td>Degradation Mechanisms in Automotive Fuel Cell Systems</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| Bipolar plates | **Press-stress, acid treatment, load cycling, temperature cycling**  
1 M H$_2$SO$_4$ + 2 ppm F, 70 °C, linear sweep: -0.5 V to 1.2 V or potentiostatic polarization: 0.1 V vs normal hydrogen electrode (NHE) for anode and 0.8 V (vs. NHE) for cathode, purged with H$_2$ for anode and air for cathode  
**Freeze-thaw cycles between -35 and 20 °C** |
| GDL | **Chemical oxidation in hydrogen peroxide (H$_2$O$_2$), elevated potential, low humidity**  
1 M H$_2$SO$_4$, under potentiostatic treatment of 1.2 V (vs. RHE)  
**OCV, 80 °C, fully humidified H$_2$ and N$_2$ for anode and cathode, 1.2 V (vs. RHE)** |
| Catalyst/catalyst layer | **Potential cycling, acid washing, elevated temperature, fuel or oxidant contaminants**  
Pt and/or Pt alloy, chemical and electrochemical stability  
80 °C, 100% RH, step change (30 s/step) in voltage from 0.6 to 0.96 V with air on cathode and H$_2$ on anode |
| Mechanical stability | **Humidity cycle: N$_2$/N$_2$, 80 °C, RH of inlet gases cycled between 0 and 100% RH every 30 min**  
**Load cycle: H$_2$/O$_2$, 50% RH, 80 °C, load cycled between 10 and 800 mA cm$^{-2}$ (7 min/3 min)** |
| Chemical and mechanical stability |  
80 °C, 100% RH, cathode 1.2 V relative to anode, with N$_2$ on cathode and H$_2$ on anode  
80 °C, H$_2$ with 226% RH at anode, with air 100% RH at anode  
80 °C, 100% RH, step change (30 s/step) in voltage from 0.6 to 0.9 V with N$_2$ on cathode and H$_2$ on anode  
20 °C, 0.5 M H$_2$SO$_4$, potentiostatic treatment 1.2 V (vs. RHE)  
40 or 80 °C, 1 M HClO$_4$, potential cycling between 0.85 V (vs. RHE) and 1.4 V (vs. RHE)  
65 °C, 100% RH, step change (10 s/step and 30 s/step) in voltage from 0.6 to 0.9, respectively, with N$_2$ on cathode and H$_2$ on anode  
Carbon support stability  
80 °C, 100% RH, potential hold at 1.2 V, with N$_2$ on cathode and H$_2$ on anode  
80 °C, 100% RH, potential hold at 1.5 V, with N$_2$ on cathode and H$_2$ on anode  
OCV, 80 °C, with partially humidified H$_2$ and air (both 66% RH) introduced to anode and cathode, start/stop cycles between H$_2$/air (45/100 sccm) for 30 s and air/air (45/0 sccm) for 20 s  
50 °C, with fully humidified 4% H$_2$/N$_2$ and He for anode and cathode respectively, 2 mV s$^{-1}$ potential cycling between 0.04 and 1.2 V (vs. RHE)  
95 °C, 80% RH, potential hold at 1.2 V, with N$_2$ on cathode and H$_2$ on anode  
GDL | **Chemical oxidation in hydrogen peroxide (H$_2$O$_2$), elevated potential, low humidity**  
1 M H$_2$SO$_4$, under potentiostatic treatment of 1.2 V (vs. RHE)  
**80 °C, fully humidified H$_2$ and N$_2$ for anode and cathode, 1.2 V (vs. RHE)** |
| **Chemical/electrochemical oxidation** |  
Di water, 60 or 80 °C, purged with N$_2$ or air 15 wt.% H$_2$O$_2$ at 82 °C  
1 M H$_2$SO$_4$, under potentiostatic treatment of 1.2 V (vs. RHE)  
**80 °C, fully humidified H$_2$ and N$_2$ for anode and cathode, 1.2 V (vs. RHE)** |
| **Mechanical stability** | **Compressive stress at 80 °C and 200 psi** |
| **Freeze-thaw cycles between -35 and 20 °C** |"
calomel electrode (SCE) for anode and 0.6 V (vs.SCE) for cathode, purged with H₂ for anode and O₂ for cathode

<table>
<thead>
<tr>
<th>Experiment Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M HCl, linear sweep: 0 V (vs. RHE) to 1.0 V (vs. RHE)</td>
</tr>
<tr>
<td>0.1 M K₂SO₄, pH 1, 80 °C, linear sweep: -0.5 V to 1.2 V or potentiostatic polarization: 0.0 V for anode and 0.6 V (vs. NHE) for cathode, purged with H₂ for anode and air for cathode</td>
</tr>
<tr>
<td>H₂SO₄ and Na₂SO₄, pH 4.8, linear polarization: -1.5 V to 1.5 V (vs. SCE), room temperature, no reactive gas</td>
</tr>
<tr>
<td>0.5 M H₂SO₄, linear polarization: -0.5 V to 0.5 V (vs. OCV), room temperature, purged with air</td>
</tr>
<tr>
<td>0.001 M H₂SO₄ + 2 ppm F, 80 °C, potentiostatic polarization: 1.0 V (vs. NHE), purged with N₂</td>
</tr>
<tr>
<td>0.001 M H₂SO₄ + 0.00015 M HCl + 15 ppm HF, 70 °C, linear polarization: -0.309 V to 0.941 V (vs. NHE), purged with H₂ for anode and O₂ for cathode</td>
</tr>
</tbody>
</table>

Sealing gasket | Temperature, acid treatment, deformation/press-stress | Chemical and mechanical stability | Bend strip environment stress crack resistance tests with various bend angles, 1 M H₂SO₄ + 10 ppm HF |
|----------------|-------------------------------------------------|---------------------------------|----------------------------------------------------------|

| 8.1. Carbon corrosion ASTs |

Research recently carried out by the Los Alamos National Laboratory group shows improvement of the correlation between the AST and field data [145]. They have used common ASTs and developed improved ASTs for the membrane and catalyst layer degradation. The newly developed AST for the carbon corrosion (1.2 V hold) is compared with the new AST with triangular sweep cycle between 1.0 V and 1.5 V, Figure 7.

---

**Table 2: Catalyst Support Cycle and Metrics**

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Hold at 1.2 V for 24 h, run polarization curve and EC/CA, repeat for total 400 h, Single cell 25-50 cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test</td>
<td>Continuous operation for 400 h.</td>
</tr>
<tr>
<td>Temperature</td>
<td>80°C</td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>Amplitude/Cycle 100/100%</td>
</tr>
<tr>
<td>Pressure</td>
<td>150 kPa absolute</td>
</tr>
<tr>
<td>Metric</td>
<td>Frequency</td>
</tr>
<tr>
<td>Catalyst activity*</td>
<td>Every 24 h</td>
</tr>
<tr>
<td>Polarization curve from Rg = 24.5 kΩ**</td>
<td>Every 24 h</td>
</tr>
<tr>
<td>EC/CA cycle</td>
<td>Every 54 h</td>
</tr>
</tbody>
</table>

* Mass activity in A/mg @ 1.50 kPa abs backpressure ± 15% mV nR-corrected vs 600°C Hg |
** Polarization curve from Fuel Cell Tech Test Polarization Protocol in Table 5 |

---

**Table 7: Catalyst Support Cycle and Metrics**

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Triangle sweep cycles: 500 mA between 1.0 V and 1.5 V, run polarization curve and EC/CA, repeat for total 400 h, Single cell 20-50 cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number</td>
<td>4000 cycles</td>
</tr>
<tr>
<td>Cycle time</td>
<td>2 seconds</td>
</tr>
<tr>
<td>Temperature</td>
<td>80°C</td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>Amplitude/Cycle 100/100%</td>
</tr>
<tr>
<td>Fuel cell</td>
<td>Hydrogen/oxygen</td>
</tr>
<tr>
<td>Pressure</td>
<td>Atmospheric</td>
</tr>
</tbody>
</table>

---

Figure 7. Old and new AST for carbon corrosion [145]

The new AST results in 150 times faster cell performance decay and roughly 100 times faster Pt particle size increase when compared to the conventional AST, Figure 8. Pt particles are decayed initially and stabilized around 5 nm as the carbon support is degraded.

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Figure 8. Comparison of ASTs for carbon corrosion: real-time holds at 1.2 V vs. AST 1.0 to 1.5 V cycling, polarization curve comparison (left) and Pt particle size vs. time (right) [145]

The newly developed carbon corrosion AST also outlines difference for the types of carbon support being used, the most stable support is EA carbon, Figure 9., AST results in 150 times faster cell performance decay and roughly 100 times faster Pt particle size increase. Pt particles are decayed initially and stabilized around 5 nm as the carbon support is degraded.

Figure 9. Polarization curve comparison of carbon support degradation for E carbon, V carbon and EA carbon under new AST. [145]

The decrease in the kinetic efficiency is a result of Pt particle sintering, while the mass transport losses are a result of catalyst layer compression and decreased porosity due to carbon corrosion, evident in electrochemical impedance spectroscopy data, Figure 10.
8.2. Membrane ASTs

Research carried out in [145] leads to conclusion that the membrane AST must be able to incorporate the influence of mechanical and chemical degradation at the same time to achieve good agreement with field data, Figure 11.

The mechanical degradation of the membrane is achieved by relative humidity cycling, which results in expansion and shrinkage of the membrane due to absorption and desorption of water, respectively. The change in membrane thickness due to relative humidity cycling, in combination with relatively high and non-uniform clamping pressure, results in increased membrane degradation rates, thinning and cracking, evident from the increased crossover rates, as seen in Figure 12. The membranes which are mechanically and chemically reinforced and stabilized show significantly lower degradation rates, as evident in the Sample B and DuPont™ XL membranes in Figure 12.
Figure 12. Crossover rates vs. time for membrane mechanical AST, reinforced membranes show significantly lower degradation rates when compared to the non-reinforced membranes. [145]

The chemical degradation ASTs are based on holding the cell at OCV for prolonged periods of time at low relative humidity of the reactants. The degradation is quite severe, a result from the increased hydrogen peroxide formation and radical attacks. After the chemical degradation AST (OCV hold, 90 °C at 30% RH), in Figure 13. left, the cathode side is completely missing after 307 hrs (left), showing more severe degradation when compared to field-testing and drive cycle data. Mechanical degradation AST (RH cycling, 80 °C, in air) has almost no effect on stabilized membranes after more than 20 000 cycles, Figure 13. right.

Figure 13. Chemical (left) and mechanical (right) degradation of DuPont™ XL membrane [145]

However, the reinforced membranes under relative humidity cycling ASTs with H₂/air (cell temperature of 90 °C and humidifiers at temperature of 92 °C, 2 mins wet, 2 mins dry) show a pronounced Pt band on the cathode side and membrane cracking even on the stabilized membranes,
Figure 14. The resulting damage from mechanical ASTs on stabilized (left – DuPont™ XL) and un-stabilized membrane (right – N211) after humidity cycling (2 mins wet, 2 mins dry).

The FCTT (2 mins wet and 2 mins dry) membrane mechanical/chemical AST, shown in Figure 15, has recently been modified by the Los Alamos National Laboratory group [146].

| Table 4: Membrane Mechanical Cycle and Metrics (Test using a MEA) |
|---------------------|----------------------|
| Cycle               | Humidity (2 mins) to 99% RH, drypoint (2 mins), single cell 25-50 cm² |
| Total time          | Unit current > 2 mA/cm² or 20,000 cycles |
| Temperature         | 80°C |
| Relative Humidity   | Cycle from 9% RH (2 mins) to 99% RH (drypoint 2 mins) |
| Flow/Oilant         | Air/Air at 2 SLPM on both sides |
| Pressure            | Ambient or no backpressure |
| Metric              | Frequency | Target |
| Crossover           | Every 24 h | < 2 mA/cm² |
| Shooting resistance  | Every 24 h | < 1,000 cm² |

| Table 3: MEA Chemical Stability and Metrics (Test using a MEA) |
|---------------------|----------------------|
| Test Condition      | Humidity (OCV), single cell 25-50 cm² |
| Temperature         | 90°C |
| Relative Humidity   | Anode/Cathode 30/30% |
| Flow/Oilant         | Humidifier at 45% RH or 2 A/cm² equivalent flow |
| Pressure            | 50(1.5) psig, Cathode 100(1.5) |
| Metric              | Frequency | Target |
| Hydrogen Crossover  | Every 24 h | < 2 mA/cm² |
| OCV                 | Continuation | 25% loss in OCV |
| High-frequency resistance | Every 24 h | < 0.2 A/cm² |
| Shooting resistance  | Every 24 h | < 500 cm² |

Figure 15. Old mechanical (left) and chemical (right) membrane degradation ASTs. [145]

The new membrane chemical/electrochemical AST has shorter, 0.5 min wet and 0.75 min dry, cycles, compared to 2 mins wet and 2 mins dry cycles in the old mechanical AST, and uses H₂/air instead of air/air configuration used in the old mechanical AST. As seen in Figure 16, the HFR peaks and valleys show good agreement with the older version of the AST, and the new mechanical/chemical AST shows comparable fluoride emissions as the old chemical AST, while it is not as severe, and shows higher degradation rates than the old mechanical AST, giving the overall better agreement with the field data than the previous separate mechanical and chemical ASTs.
One of the important parameters affecting the membrane durability is the operating temperature and relative humidity. In Figure 17, it can be easily seen that by lowering the operating temperature and relative humidity the membrane lifetime can be increased, however for ASTs it is better to keep the temperature and RH high to achieve faster degradation.

8.3. Catalyst layer ASTs

The catalyst layer ASTs represent potential cycling between the lower and higher potentials at higher temperatures and usually 100% relative humidity. Such operating conditions are prescribed to exacerbate the degradation of the electrochemically active surface area (ECSA) and the objective is
to achieve 40% loss in ECSA in as low cycles as possible. In Figure 18, a comparison is made between the conventional catalyst layer ASTs, the FCTT drive cycle and the new AST [146]. The FESB protocols for EK single-cell and BASF membrane shows slower degradation rate when compared to other ASTs due to lower operating temperature during cycling (65 °C), a result from the experimental configuration setup, as well as the fact that different membranes are used (EK and BASF membrane, compared to the DuPont™ XL membrane used in the Old and New ASTs) and at the current state the ECSA loss of 40% is not achieved during first 10000 cycles. In a future study the New AST protocol can be adopted to result in higher degradation rates in a fraction of time. The New AST results in 40% ECSA loss after ca. 3700 cycles, or in ca. 7 hours testing time.

![Figure 18](image1.png)

Figure 18. Comparison of the FESB protocol for ElringKlinger™ Single-Cell, FESB protocol BASF membrane, and New and Old ASTs and FCTT drive cycle vs. Number of cycles (left) and testing time (right). Old AST: 0.6 V to 1 V, 50 mV s⁻¹ @ 80 °C and 100% RH, New AST: Square wave 3 s 0.6 V and 3 s 0.95 V @ 80 °C and 100% RH. New and Old AST data adopted from [146].

The upper potential of 1.0 V was decreased to 0.95 V in the New AST to reduce the carbon corrosion, while retaining the Pt particle growth to similar extent as in the previously used. The New AST was adopted by the group from the literature study [147]. The details of the Old AST are shown in Figure 19.
Not only the fuel cell stack components degrade or can fail during operation, but the BoP components may degrade/age with time or with operation or they may just fail. In either case their ageing or failure could affect the fuel cell stack and system performance, and that is why it is important to address their ageing and evaluate how it can affect the Giantleap fuel cell system. The components that may be most prone to ageing or failure are the air compressor and the humidifier, both a part of the air supply line.

9.1. Factors responsible for ageing

Analysis of the components and literature research found different factors responsible for ageing. These may be classified into mechanical, chemical and thermal influences. Fig. 20 shows all the possible factors responsible for ageing of an air compressor, and Fig. 21 shows all the possible factors responsible for ageing of a humidifier.
9.1.1. Mechanical factors

Intake air polluted with particles

For the compressor, particles < 10µm might lead to fouling, agglomeration of those particles on the rotor blade surfaces. This will cause deterioration of the aerodynamic properties of the air compressor, imbalance of the rotor and thus higher structural load towards materials and bearings. Larger sized particles will cause erosion and wear on surfaces exposed to the air flow. In addition to the consequences mentioned above concerning aerodynamic and mechanical properties, this might
also cause increased contamination of other components further down the air path, including the fuel cell stack itself [145-151].

Within the humidifier, particles of any size will encourage clogging or the membrane’s pores, so performance will deteriorate.

**Vibration and shock**
Since the Components will be mounted in a vehicle operated on public roads, they will be exposed to vibration and shock caused by outside stimuli as well as by sources within the system itself. This will enhance wear of bearings and fatigue in structural components, leading to performance loss up to mechanical destruction of the component [152-156].

**Rotating stall**
Depending on the pressure necessary, the compressor might be operated very close to its surge line. This can lead to rotating stall, which will induce oscillation in the rotor blades. In addition to a loss of performance, material fatigue and increased wear of bearings can be caused [157-158].

**Rotary oscillation and resonances**
Oscillations caused by rotor imbalance, resonances as worst case, will cause increased wear of bearings and fatigue in structural components [159].

**Pressure differences**
In addition to surging and rotating stall, pressure differences can cause cavitation. This effect can cause massive erosion in components pumping liquids. For gaseous media cavitation does not occur, so this effect can be neglected for the compressor.

For the humidifier, however, pressure differences will put stress on the membranes. Over time this could cause internal leakage as well as a decline of performance.

**Oil contamination**
Since the Rotrex compressor contains roller bearings that are lubricated by oil, oil contamination needs to be considered. Mechanically, oil contamination can increase wear in bearings. Additionally, particles could cause clogging of the oil cooler [160-161].
9.1.2. Chemical factors

**Oil contamination**
In addition to mechanical wear, oil contamination with aggressive chemical substances could enhance corrosion within bearings, transmission oil pump etc. As a consequence, performance will drop due to higher friction losses. If seals are affected, traction oil might be spilled into the air path, affecting other components [160-161].

**Gaseous contamination**
Aggressive chemical substances might cause corrosion or decrease of material properties in components that are in contact with the intake air.

**Soiling**
In addition to mechanical effects, soiling of components, especially rotor blades, might induce corrosion of those components [162-163].

9.1.3. Thermal factors

**Temperature**
In terms of thermal effects, very high and very low temperatures need to be considered. While low temperature effects high viscosity of the compressor’s traction oil and thus insufficient lubrication, high temperature might generate chemical and physical degradation of the oil itself.

For the humidifier, low temperature can cause freezing of trapped humidity and so crack the structure of the membranes. Temperatures too high will damage the structural integrity of the material itself, changing the properties in terms of diffusion or even burning or melting the fibers [161, 164-167].

9.2. Evaluation of ageing mechanisms

All the theoretically possible factors for ageing from literature research have been weighted according to the conditions of the intended use, i.e., inside the range extender trailer, and the results are shown in Figure 22 for an air compressor and Figure 23 for a humidifier.
9.2.1. Mechanical factors

Intake air polluted with particles

Both manufacturers, Rotrex and Fumatech, ask for air filtration, so that no particles larger than 5µm can enter the air path.

For an urban environment, smaller particles will be relevant. For the testing will take place within an urban / industrial environment, no further measures are considered relevant.

Vibration and shock

Vibration and shock are relevant factors for the ageing of any automotive component. Stimulation by induced by the operation on public roads, however, are considered to be mainly relevant for material failure and rather less for performance losses over lifetime. Considering time and cost, the initial testing will be performed without outside stimulation of vibration or shock, with the option to do some testing afterwards.
Rotating stall
While rotating stall should be avoided by a suitable operating strategy, operating points close to the surge line will be included in the testing.

Rotary oscillation and resonances
During testing the compressor will be run in different operating points. It is not expected to strike resonances during normal operation.

Pressure differences
Pressure differences are considered critical towards the compressor while being operated safely between surge and choke lines. For the humidifier, pressure differences are considered relevant and will be reproduced by the test arrangement.

Oil contamination
Oil contamination, mechanical and chemical, are widely seen as most critical regarding ageing and failure of automotive turbo compressors. Main source for contamination, however, normally is the internal combustion engine, sharing the same oil circuit at very high temperatures > 150°C.

Since in Giant Leap, the Rotrex oil circuit is proprietary, separate, filtered, and operated at a rather low temperature level, contamination of the oil circuit is not considered a major problem for this use case.

9.2.2. Chemical factors

Oil contamination
Oil contamination is not considered critical for Giant Leap, see 9.2.1. above.

Gaseous contamination
Since the fuel cell stack is most critical regarding Gaseous contamination, a chemical (charcoal) filter is required for the air system. Hence gaseous contamination will not be critical for air path components.

Soiling
Beyond clogging of pores and fouling of rotor blades because of smallest particles, especially for the humidifier biological contamination might become a factor for performance losses. Operation and standstill at high humidity and high temperatures will be covered by the testing procedure.
9.2.3. Thermal factors

Temperature

In the Giant Leap system, all components will be run well within their specifications. For the compressor, mainly very cold oil temperatures are considered relevant for wear. For the humidifier, cold temperatures will be relevant in terms of freezing, hot temperatures regarding material properties and fatigue. During the testing procedure, a temperature range between -30 and 110°C will be covered.

10. Conclusions

Degradation mechanisms in automotive fuel cell systems are systematically shown along with brief description of the underlying mechanisms leading to degradation and/or early failure of the main structural components. Mitigation strategies are outlined for each component separately, with emphasis on mitigation strategies based on the influence of the operating conditions on increasing the stability and reliability of the system. The complexity and inter-relation of different degradation mechanisms during operation makes it difficult to design a reliable AST which will be able to encompass all of the degradation mechanisms in the extent comparable to the field testing.

The analysis and evaluation of the mechanical, chemical and thermal factors contributing to ageing and/or early failure of the balance-of-plant components, particularly the air compressor and the humidifier, identified the most critical ageing factors for the conditions of the intended use, i.e., inside the range extender trailer, and identified those that will need to be characterised in laboratory experiments.
References


[152] S. S. Manson, A. J. Meyer und e. al., „FACTORS AFFECTING VIBRATION OF AXIAL-FLOW COMPRESSOR BLADES“, National Advisory Committee for Aeronautics, Cleveland.


