

## Experimental Investigation of Degradation Mechanisms in a Range Extender PEM Fuel Cell System

*Experimentelle Untersuchung von Alterungsmechanismen in einem Range Extender PEM Brennstoffzellensystem*



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### Abstract

*This publication gives an overview of the degradation behaviour of membrane-electrode-assemblies (MEA) of proton exchange membrane fuel cells (PEMFC). The focus lies on the degradation of the carbon electrodes, the platinum catalyst and the ionomer membrane. The results gained by different measurement strategies and methods to investigate fuel cell degradation of a stack in system test bed operation are introduced. The formation of gaseous CO<sub>2</sub> due to carbon corrosion is detected by gas measurement in the fuel cell exhaust and the development of the cell voltage level at reference measurements is analysed. A reduced pressure resistance and an elevated hydrogen concentration level in the exhaust indicate membrane degradation. Furthermore, a reduced open cell voltage of the individual MEAs during shutdown and a shorter voltage bleeding time caused by MEA degradation are detected. A comparison of the polarization curves reveals the overall system degradation of 145  $\mu\text{V}/\text{h}$  or 12  $\text{mV}/\text{MWh}$  at high current densities.*

### Kurzfassung

*Diese Veröffentlichung gibt einen Überblick über das Degradationsverhalten der Membran-Elektroden-Einheiten von Polymerelektrolytmembran (PEM) Brennstoffzellensystemen mit dem Schwerpunkt Degradation der Kohlenstoffelektroden, des Platinkatalysators und der Ionomer-Membranen. Die Ergebnisse unterschiedlicher Messstrategien und -methoden eines Stapels im Systemprüfstandbetrieb werden vorgestellt. Durch den Anstieg der CO<sub>2</sub>-Konzentrationen im Abgas kann Kohlenstoffkorrosion nachgewiesen werden und die Entwicklung der Zellspannungen in Referenzmessungen wird analysiert. Eine reduzierte Druckbeständigkeit und eine höhere gemessene Wasserstoffkonzentration im Abgas sind Folgen der Membranalterung. Weiters kann eine reduzierte offene Zellspannung der einzelnen MEAs im Stapel und ein verzögertes Absinken der Zellspannungen während des Abschaltvorganges durch Degradation der MEAs nachgewiesen werden. Der Vergleich der Polarisationskurven zeigt die Systemdegradation von 145  $\mu\text{V}/\text{h}$  oder 12  $\text{mV}/\text{MWh}$  bei hohen Stromdichten.*

## 1. INTRODUCTION

The use of fuel cells in mobile applications is a promising technology for sustainable decarbonisation. A major aspect of fuel cell research focuses on limiting the system degradation to achieve a higher stack lifetime with minor power losses and the most possible avoidance of total system failures. Therefore, this publication is dedicated to the experimental investigation of fuel cell system degradation.

### 1.1. The Fuel Cell System

The proton exchange membrane fuel cell (PEMFC) system converts hydrogen and air into electricity, water and heat. The PEMFC system is designed as a range extender for battery electric public transport applications and delivers a rated electric power of 25 kW. The open-cathode system has graphitic bipolar plates and is operated without reactant humidification. The fuel cell system consists of the fuel cell stack, anode module, cathode module, cooling module and power electronics. The auxiliary components are called balance of plant (BoP) components. In the fuel cell stack, the single cells are arranged in series to reach the desired voltage level. The power electronics convert the stack voltage to the high-voltage level and set the current demand. The anode module adjusts the hydrogen pressure to the appropriate level, controls the hydrogen mass flow, and contains safety switches and valves to ensure a safe operation. Furthermore, it operates the purge and drain valves. During fuel cell operation, nitrogen and water permeate from the cathode to the anode, resulting in a reduced hydrogen partial pressure, causing a reduced fuel cell performance and in the worst-case electrode corrosion due to fuel starvation [1]. To remove the cumulated nitrogen and water, the anode is purged and drained frequently, causing a certain hydrogen loss during the process. The cathode module consists of an air filter and the air compressor, followed by a heat exchanger to cool the air heated by the compression. The fuel cell is cooled by an optimally adapted coolant liquid, flowing through the bipolar plates.

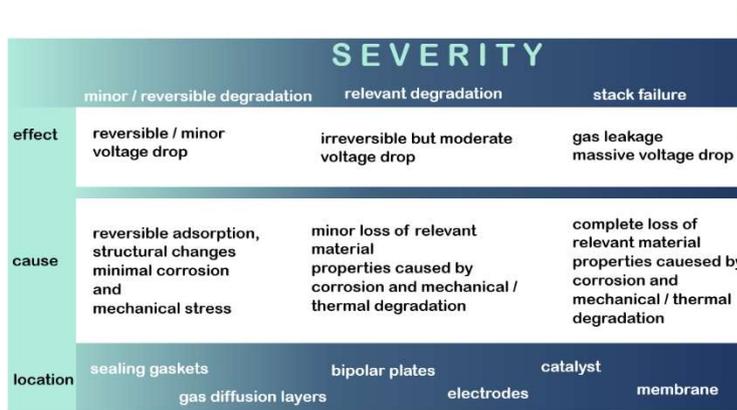
The test bed at IVT has the appropriate infrastructure for operating hydrogen fuel cell systems of up to 150 kW electrical power and a test bed automation system. The gas measurement equipment in the exhaust of the fuel cell includes a mass spectrometer for measuring the hydrogen concentration (based on electron pulse ionization) and an infrared detector for measuring CO<sub>2</sub>.

## 2. PEM FUEL CELL DEGRADATION

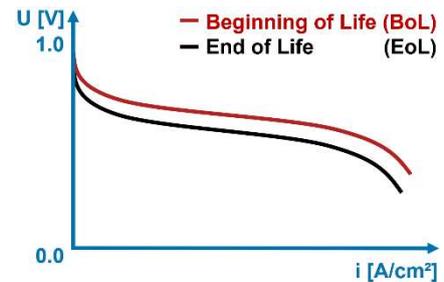
This chapter gives an overview of effects, causes, and the location of degradation within a PEMFC. The observation and the understanding of degradation phenomena is the point of interest of this study and the evaluation by means of experimental verification like in [2]. During operation, the PEMFC is subjected to degradation like all energy converters. The main effect of degradation is a reversible or irreversible voltage loss during the operation caused by changes in the material properties. Although a clear identification of the primary causes leading to specific degradation is not possible in many cases, degradation can be divided into three main categories:

- Degradation caused through mechanical forces and thermal stress
- Degradation induced through reversible adsorption and desorption of ions or molecules on or within the material
- Degradation through electrochemical and chemical material reduction or conversion

Whereas an inevitable stack voltage drop resulting from degradation can be minimized to a certain extent, stack failure induced by major degradation effects within the expected lifetime has to be avoided by all means. Typical voltage losses during normal operation of automotive systems are in a range of 2 – 10  $\mu\text{V}/\text{h}$  and a power loss of 10 % at the so-called end-of-life (EoL) compared to the beginning of life (BoL) of a fuel cell is commonly accepted (see **Figure 2**) [4]. Depending on the severity of the degradation mechanism and the affected location, the consequences shown in **Figure 1** might occur.



**Figure 1:** Overview of degradation effects, causes and affected parts in a fuel cell [3]



**Figure 2:** Polarization curve of a fuel cell at BoL and EoL

## 2.1. Degradation mechanisms

Degradation triggered by electrochemical reactions is favoured by applied load, elevated or change of temperature and humidity, the presence of oxygen and hydrogen, and a strongly acidic environment. These conditions are prevalent in PEMFC during operation, leading to a certain extend of corrosion of the membrane, the electrode material and the catalyst as the major cause for PEMFC degradation.

### 2.1.1 Membrane degradation

The common membrane materials for PEMFC are perfluorosulfonic acid (PFSA) ionomers, which are mainly degraded and thinned by hydrogen peroxide radicals. These peroxide radicals are formed in-situ in the presence of both hydrogen and oxygen on the platinum catalyst at cell potentials lower than 0.695 V. They are most stable at the anode side at open cell voltage. High temperatures, low membrane humidity and the presence of metal ions (mainly  $\text{Fe}^{2+}$ ) accelerate corrosion. Highly corrosive conditions can lead to pinhole formation and result in severe stack failure through local combustion of hydrogen and oxygen. Additionally, mechanical and thermal stress are further reasons for membrane degradation. [5]

### 2.1.2 Carbon corrosion

Principally, carbon is not stable at potentials higher than 0.207 V in an acidic environment, but the formation of  $\text{CO}_2$  is kinetically sufficiently inhibited for the use as PEMFC electrode material, even at the cathode side. However, the presence of platinum and high temperatures decreases the kinetic inhibition, so that measurable carbon corrosion at the cathode can occur during the fuel cell operation. In addition, hydrogen peroxide radicals might cause carbon corrosion at the anode side.

A special cause of carbon corrosion is the insufficient supply of hydrogen at the anode, leading to a high oxygen permeation through the membrane. In the case of potentiostatic operation, oxygen is reduced to water at the anode at high potentials. The cathode potential is forced to high potentials that enable uninhibited electrochemical oxidation of the carbon electrode material. In the case of galvanostatic operation, the potential at the anode increases and therefore enables the oxidation of water to oxygen and the oxidation of carbon. [6, 7]

### 2.1.3 Catalyst degradation

The direct platinum oxidation with a standard potential of 1.188 V is not a relevant degradation mechanism for fuel cell operation. Platinum degradation occurs via the Ostwald-ripening mechanism, the dissolution of platinum particle surface PtO at a potential higher than  $\sim 0.8$  V and the subsequent platinum redeposition on electrically conducted particles. Although there is no material loss, the active catalyst surface decreases, leading to a lower electrochemically activity of the cathode. [7]

## 2.2. Identification of degradation

Degradation can be detected qualitatively and quantitatively using different in-situ, in-operando and ex-situ analysis methods. In-situ and in-operando analysis during the PEMFC operation enables the identification of individual degradation effects in the long term. Ex-situ analysis, including post mortem analysis, enables a deeper understanding of the degradation mechanism and links the gained measurement data from the operation with defects within the fuel cell. For the validation of the measurements during operation it is suggested to perform the following tests in the initial operation phase for a basic reference. The evaluation of the basic condition is performed by a standardized conditioning phase which guarantees stationary humidity conditions within the MEA. In addition, it is necessary to perform the tests at similar environmental conditions to gain reproducible test results. A classic tool for the observation of the state-of-health (SoH) of a fuel cell is the use of a cell voltage monitoring (CVM) system. The CVM measures the cell voltage of single cells or cell packages during the fuel cell operation. [2]

- The SoH can be evaluated by measuring the open cell voltage (OCV). At the **OCV test**, the anode and the cathode are supplied with reactant gas without drawing current.
- After an OCV test, additional information about the SoH is gained through the **bleeding test**. Thereby, the gas supply is stopped and the decrease of the cell voltages is observed.
- Measuring the **polarisation curve** of a fuel cell is a standard procedure to gain the SoH.
- Performing internal **leakage tests** of the fuel cell provides information on the physical condition of the membrane.
- Measuring **pressure losses** over the stack on the anode as well as at the cathode leads to information about blocked flow channels resulting from improper water management.
- Further degradation products can be identified by **exhaust measurements** and **product water analysis**.
- By **observation of the stack outlet temperatures** efficiency losses and present or evolving pinholes can be detected.
- **Ex-Situ analysis** of degraded fuel cells gives information about cracks, delamination and changes in material properties.
- **Total harmonic distortion analysis (THDA)** and **Electrochemical impedance spectroscopy (EIS)** are using an interfering signal on the cell voltage and detection of the resulting cell voltage. These measurements allow an exact identification of the smallest changes in the fuel cell operation.

## 2.3. Optimisation / Minimization / Avoidance of degradation

An optimized operation strategy and operating conditions of a fuel cell can minimize degradation and increase the lifetime expectancy. **Table 1** gives an overview of optimal operation strategies for a PEMFC. [2]

**Table 1:** Overview of optimal operation strategies for a PEMFC [2]

Requirements for the load profile	Controllable operation conditions of the stack	Minimization of harsh environmental conditions
Voltage should be in the linear range of the polarization curve	Constant humidification and fully humidified membrane	Avoidance of high mechanical stress
Avoidance of low current densities and long operation at OCV	Full removal of product water	Avoidance of freezing stack and cell
Avoidance of high current densities	Constant, moderate temperature, low temperature gradients over anode, cathode and coolant	Moderate environment temperature
Minimization of start-up and shut-down cycles	Over stoichiometric gas supply and gas recirculation, constant gas pressure	Vibrations
Minimization of thermal cycles	Optimised start-up and shutdown phase (Avoidance of Air / Air start)	Pollutants

### 3. EXPERIMENTAL IDENTIFICATION OF DEGRADATION

The results presented in this paper are all gained by in-operando measurements, which means that the fuel cell is operated while the measurements are made. By performing repeatable experiments, the measured data can be used to evaluate changes in the fuel cell behaviour and conclusions can be drawn regarding the most probable degradation mechanism.

As mentioned before, the fuel cell operating parameters need to be comparable among the tests. This includes the membrane water content, pressure, temperature, relative humidity and flow rate of the reactants and the stack coolant temperature. An appropriate preconditioning phase of the system and steady-state operation enables these conditions.

The considered testing period in this publication accounts for 192.7 hours of operation and 2.36 MWh delivered electric energy. It is marked by a polarization curve at the beginning of tests (BoT) and one at the end of tests (EoT). Before BoT, the fuel cell system was operated at different test beds for 122.6 hours, delivering 1.67 MWh of electric energy. The considered testing period includes experiments with cathode gas pollutants. The pollutants affect the cathode catalyst activity hindering the ORR and thus accounting for a recoverable voltage degradation [8]. The reversibility of the voltage degradation allows an overall degradation analysis over the testing period.

#### 3.1. Fuel cell start-up and shutdown

The fuel cell control unit (FCCU) follows predefined strategies for the fuel cell start-up and shutdown. During start-up, the anode leakage test is used for degradation evaluation. At fuel cell shutdown, the OCV test, the voltage bleeding process and the pressure drop rate at the anode are considered. During the OCV and leakage tests, the anode and cathode are supplied with reactants, but no external current is drawn. The voltage bleeding process is done by shutting off the reactant supply, which causes the cell voltages and media pressures to decrease. The evolution of the cell voltage decrease gives information about the SoH of the fuel cell. The anode pressure drop during the leakage test and the voltage bleeding process shows the mechanical condition of the membrane.

During the start-up of the fuel cell, the fuel cell operating parameters can't be controlled and depend on the preceding events. These include the experiments and load profiles of the previous test, the shutdown procedure and the duration of no operation. It is therefore relevant to choose comparable preliminary conditions when using the fuel cell start-up for evaluating degradation. Reference starts are identified at

which those criteria are fulfilled. The measurements during the shutdown procedure are also influenced by the preceding fuel cell operation, making it important to choose valid tests for the evaluation.

### **3.2. Steady-State operation at a reference load point**

The steady-state operating point at medium fuel cell load is performed at the beginning of every experiment following a defined procedure. Due to the repeatability of the process, the fuel cell operating parameters are assumed to be comparable among different experiments. The load point is held constant for 30 minutes. The measured data of the last ten minutes are averaged for the degradation evaluation.

### **3.3. Reference cycle**

After the previously described preconditioning phase, an ascending and descending load ramp is performed. This load ramp is a tool to evaluate the system performance between tests and to investigate the fuel cell system condition at the time of the experiment. Since the load ramp is performed equally over the whole testing time, it can be used to evaluate the system degradation by averaging the measured data over the cycle period.

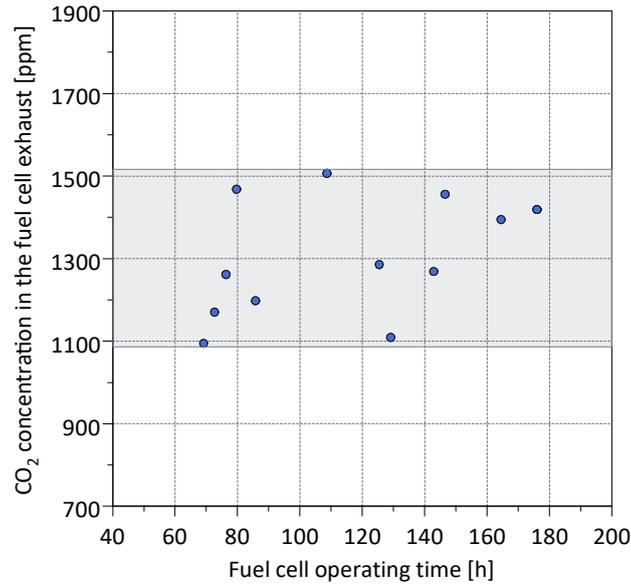
### **3.4. Polarization curve**

The fuel cell polarization curve is one of the most fundamental methods to evaluate the system SoH. It is used to determine the system capabilities and is often the data basis for parameterizing simulation models and calculations. The polarization curves at BoT and EoT are used to evaluate the overall system degradation during the testing period. The polarization curve is recorded while consecutive load points in 25 A steps are held constant for ten minutes each. An appropriate dwell time at each load point ensures, that the fuel cell parameters reach a steady-state condition. This makes it possible to compare curves recorded at different system lifetimes.

## **4. METHODS FOR ANALYSING FUEL CELL SYSTEM DEGRADATION AND RESULTS**

### **4.1. Detected carbon corrosion**

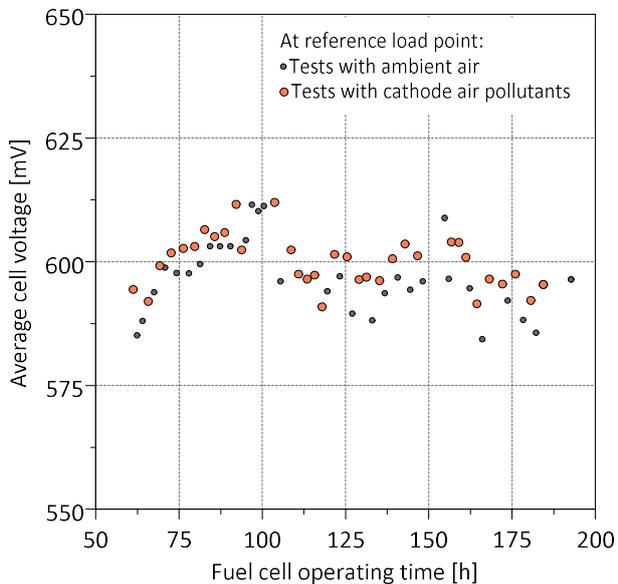
As described in Chapter 2.1.2, carbon corrosion causes the formation of gaseous CO<sub>2</sub> that can be detected in the fuel cell exhaust by gas measurement. Carbon corrosion can take place during the shutdown process and the start-up process of the fuel cell and can originate from both cathode and anode. Under normal fuel cell operation, no increased CO<sub>2</sub> concentration in the exhaust is detected. The start-up process leads to significant CO<sub>2</sub> concentrations in the cumulated exhaust gas of the anode and the cathode. The shutdown process does not cause detectable CO<sub>2</sub> emissions. **Figure 3** shows the CO<sub>2</sub> level measurements at the reference starts (described in Chapter 3.1). The values don't show a clear decreasing or increasing tendency, but vary within a range. The carbon corrosion rate can reach a certain level during the fuel cell life time, after an increased rate at the beginning of fuel cell life [9]. This level could be the case in the presented results. The measurements, however, don't include the carbon corrosion rates from the beginning of fuel cell life. Therefore, a conclusion of the development of carbon corrosion during the testing time can't be drawn. During data evaluation it can be observed, that the fuel cell operating conditions at start-up and shutdown influence the level of CO<sub>2</sub> in the exhaust.



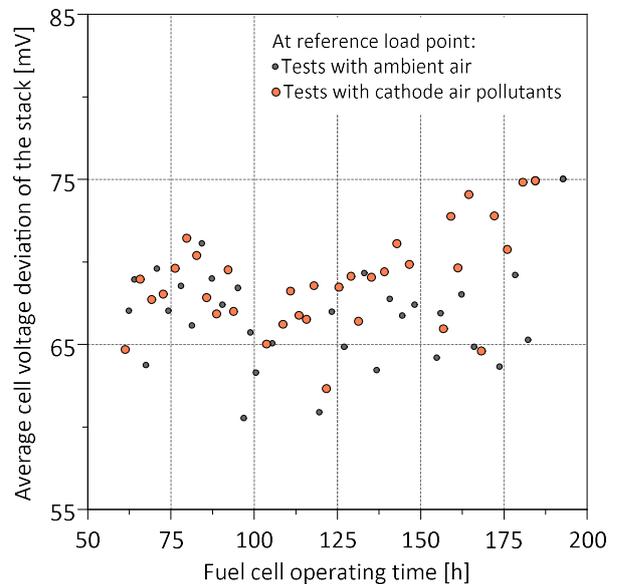
**Figure 3:** Measured CO<sub>2</sub> concentration in the fuel cell exhaust at reference starts

#### 4.2. Evolution of cell voltage and voltage distribution

As described in Chapter 2.2, the cell voltage is commonly used for degradation evaluation. Due to the influences of fuel cell operating parameters on the cell voltages, it is crucial to choose representative tests with comparable operating conditions. The steady-state operation at the reference load point (see Chapter 3.2) fulfils these requirements. The average cell voltage of the fuel cell stack and the average deviation between maximum and minimum cell voltage within the stack are evaluated in these reference points.



**Figure 4:** Average cell voltage at the reference load point



**Figure 5:** Average cell voltage deviation at the reference load point

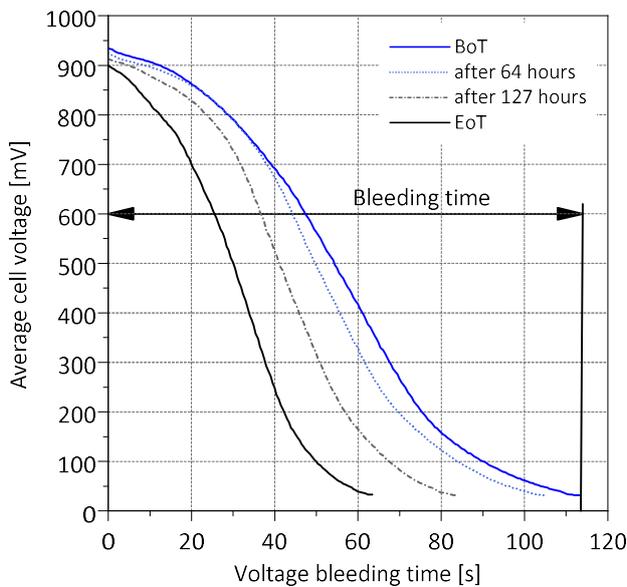
**Figure 4** shows the average cell voltage of the stack and its significant variation within the operating time. This effect is caused by the previously described experiments with cathode air pollutants, which are performed periodically and with varying concentrations and exposure times throughout the fuel cell operating time. These tests are marked in orange in **Figure 4** and **Figure 5**. The reference load point is performed before the air pollutant exposure, so only the subsequent test is influenced. The varying cell

voltage recovery rates between the experiments further influence the uneven distribution of the measured cell voltages and the average cell voltage deviation between the minimum and maximum cell voltage within the stack (see **Figure 5**).

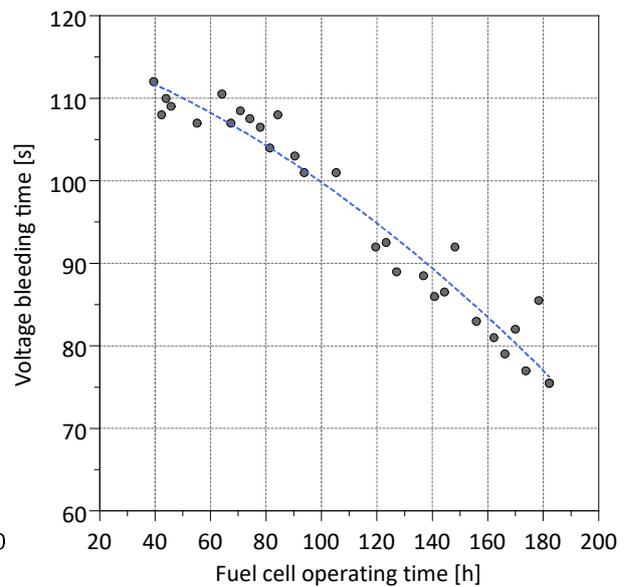
### 4.3. Identification of membrane degradation

#### 4.3.1 Analysing data from start-up and shutdown

The voltage bleeding process (as described in Chapters 2.2 and 3.1) is monitored by measuring the cell voltages. The voltage bleeding curve of individual cells or cell packages gives information about their individual SoH. For presentation purposes, **Figure 6** only shows the average cell voltage of all measured cells. It can be seen, that the bleeding time decreases during the testing period between BoT and EoT. Two additional measured curves are included in the graph, to describe the evolution of the bleeding behaviour. One of them is recorded after 64 hours of testing time and the other one after 127 hours. This represents roughly one-third and two-thirds of the overall testing time. The voltage curve after 64 hours shows a lower deviation to BoT than the curve after 127 hours. **Figure 7** depicts the evolution of the bleeding time after representative fuel cell operation, indicating a decreasing tendency. It has to be mentioned, that **Figure 7** does not contain the bleeding times of all experiments conducted during the testing period, since occasional irregular shutdowns and strongly differing load profiles are not included in the evaluation.



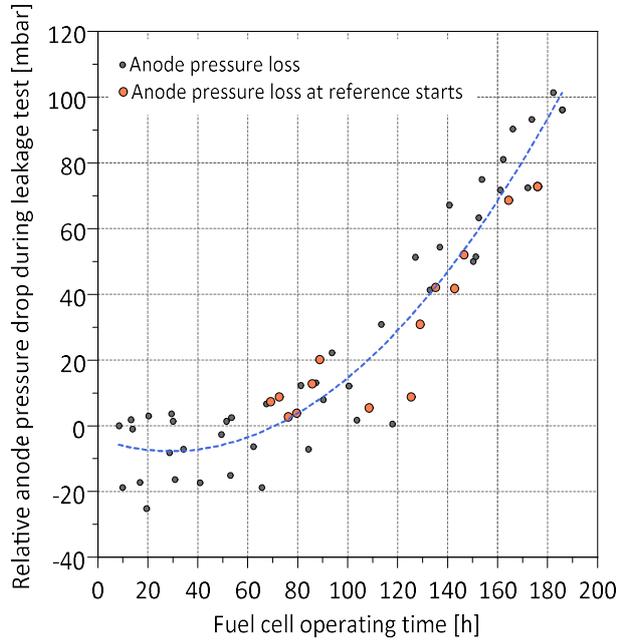
**Figure 6:** Cell voltage bleeding curves at different testing times



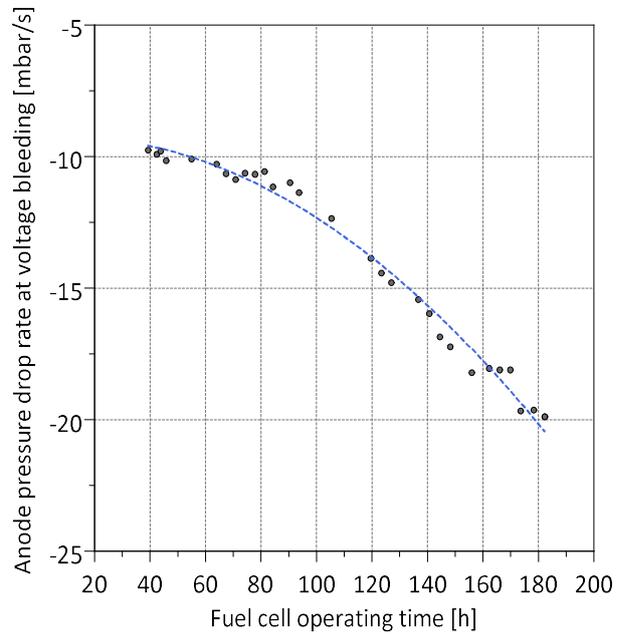
**Figure 7:** Evolution of the voltage bleeding time during the testing period

The leakage test described in Chapter 3.1 is used for evaluating the anode pressure drop during this phase. A successful leakage test shows that the membrane SoH is sufficient and that no other leaks in the fuel cell stack occur. For security reasons, the stack housing and the test bed are equipped with hydrogen sensors. These sensors don't detect a hydrogen leak in the stack caused by the increasing anode pressure drop during the testing time in **Figure 8**. The hydrogen concentration in the exhaust, on the other hand, increases gradually over the testing time. This observation leads to the conclusion that the hydrogen pressure decreases due to crossover through the membrane to the cathode, where it is detected in the gas stream. Therefore, the pressure drop during the leakage test is seen to be a suitable measure for monitoring the propagating membrane degradation.

**Figure 8**, therefore, indicates a decreasing pressure resistance of the membrane caused by thinning or pinhole formation (described in Chapter 2.1.1). **Figure 8** shows a relative increase in the pressure drop magnitude, based on the first valid measurement in the testing time. The validation of each measurement is carried out by a regular run-through of the start-up process. Additional to the regular start-up procedures, the measurements from the reference starts (described in Chapter 3.1) are highlighted in orange.

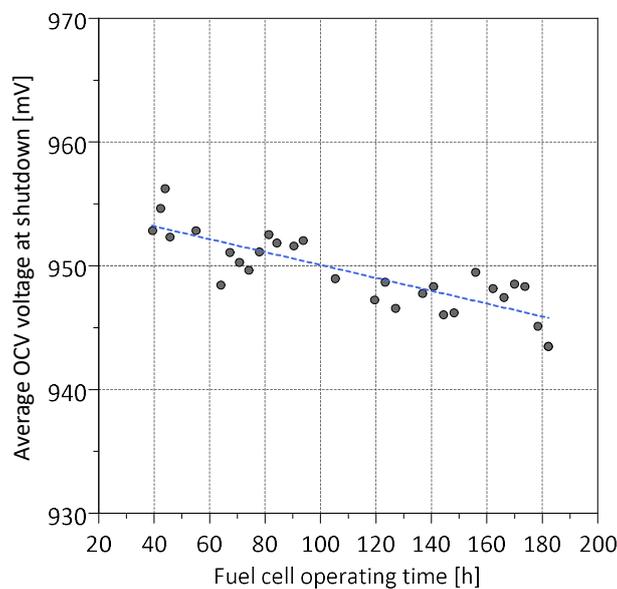


**Figure 8:** Anode pressure drop during the leakage test



**Figure 9:** Anode pressure drop rate during voltage bleeding

A similar observation can be made during the fuel cell shutdown process. The anode pressure decreases during voltage bleeding, which is theoretically mainly caused by the consumption of the remaining reactants. An increased hydrogen pressure drop during an otherwise unchanged bleeding process, however, indicates a reduced pressure resistance of the membrane. Similar to the leakage test, no exceeding hydrogen concentration in the fuel cell stack or at the test bed is detected. Due to the missing air mass flow during the bleeding process, the hydrogen concentration measurement in the exhaust is not possible. **Figure 9** shows the increasing pressure drop rate over the testing period.

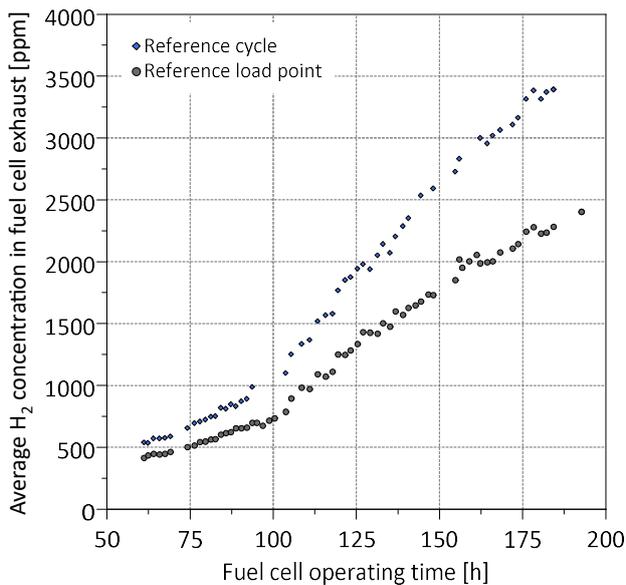


**Figure 10:** OCV during fuel cell shutdown

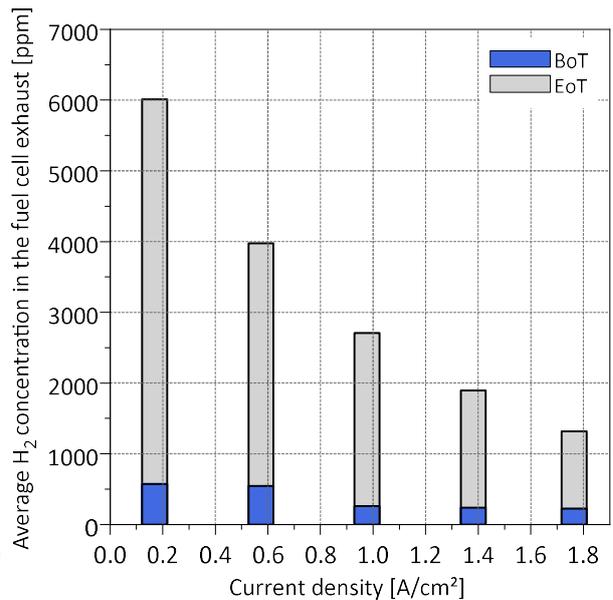
Since no other reason for the decrease in pressure drop could be identified and the trend over the testing time matches with other observations, the nearest conclusion is that the membrane degradation enables the hydrogen to cross over to the cathode at an increased rate. The measurements depicted in **Figure 9** don't include all tests, since irregular fuel cell shutdowns can't be included in the evaluation. A reduced OCV level is another indicator for increased gas permeation through the membrane [9]. The OCV at fuel cell shutdown (see Chapter 3.1) at the end of comparable cycles ensures similar fuel cell operating conditions. **Figure 10** shows the results of this shutdown OCV analysis, indicating a decreasing tendency. The previously described influence of hydrogen crossover on the OCV level is considered to be the main cause of this development.

#### 4.3.2 Analysing data recorded during fuel cell operation

The previously discussed evaluation methods depend on predefined routines or steady-state operating points. Evaluating the cell voltage degradation or changes in pressure levels during a reference cycle (described in Chapter 3.3) is not practical. The changing fuel cell parameters during the cycle such as media temperatures, pressures and humidification influence the cell voltage strongly. A method to assess membrane degradation during transient fuel cell operation is measuring the hydrogen concentration in the fuel cell exhaust. A post-processed signal excluding the concentration peaks during anode purge and drain can be compared throughout the tests. **Figure 11** shows the increase of the average hydrogen concentration in the exhaust during the reference cycle (Chapter 3.3) in blue.



**Figure 11:** Average H<sub>2</sub> exhaust concentration at the reference load point and during the reference cycle



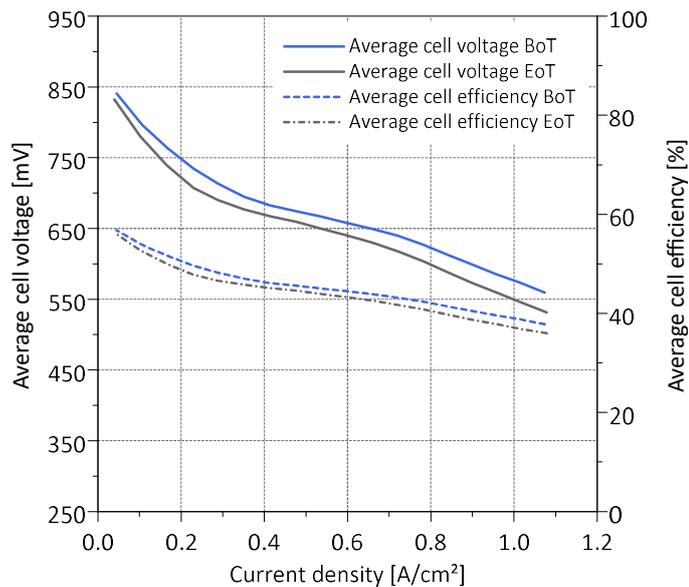
**Figure 12:** Average H<sub>2</sub> exhaust concentration at load points of the polarization curve

A moderate increase at the beginning is followed by a more rapid inclination of the hydrogen concentration, indicating a non-linear membrane degradation. This is most likely caused by the experiments with cathode gas pollutants. The difference between the results of the reference cycle and the reference load point can be seen in **Figure 11**. The hydrogen concentration of the reference load point increases less strongly, which indicates an influence of the varying load points. This is substantiated by **Figure 12**, depicting the average hydrogen concentration level during stationary load points of the polarization curves at BoT and EoT. The concentration increase is profoundly bigger at low current densities, caused by the varying pressure difference between cathode and anode. The cathode pressure depends on the compressor mass flow but the anode pressure is kept constant by the FCCU. Therefore, the higher pressure gradient between anode and cathode results in an increased crossover through the degraded membrane.

#### 4.4. Overall system degradation

##### 4.4.1 Change of the polarization curve due to system degradation

The polarization curve is performed as described in Chapter 3.4. The curves at BoT and EoT are displayed in **Figure 13**. The shape of the polarization curve is caused by different losses during fuel cell operation. The first region of decreasing cell voltage, starting at low current density, is dominated by activation losses. The ohmic losses are the prevailing source of voltage loss in the second, almost linear region of the polarization curve. Towards higher current densities, the diffusion losses due to limited gas exchange are predominant, causing a more pronounced decrease of the voltage curve than in the previous region [10].



**Figure 13:** Polarization curve and cell efficiency at BoT and EoT

In terms of degradation, several conclusions can be drawn from the shape of the polarization curve. The EoT curve shows an almost parallel offset to the BoT curve caused by increased gas permeation through the membrane and the increased internal current densities. Further, the additional voltage drop at low current densities indicates higher activation losses, caused by carbon corrosion and platinum agglomeration in the active layer degradation [11]. The voltage drop in the current density range between 0.25 A/cm<sup>2</sup> and 0.8 A/cm<sup>2</sup> is low, indicating both a constant membrane conductivity and constant contact resistances within the stack during its total testing period. The voltage drop at higher current densities and dominant diffusion losses indicates, that the hydrophobic properties of the MEA and the gas diffusion layer (GDL) degraded over the testing period. This impairs the gas exchange and product water removal in these layers and reduces the fuel cell performance [12] [11].

The cell voltage efficiency curve in **Figure 13** shows the ratio between the average cell voltage of the stack and the thermoneutral ideal cell voltage [10]. The shape of the curve resembles the one of the polarization curve and indicates a decrease of 1.9 % in cell efficiency at the highest current density.

By analysing the difference in cell voltage of the polarization curve at the highest current density between BoT and EoT, a significant cell voltage loss over the testing period can be derived. This amounts to roughly 145  $\mu$ V/h or 12 mV/MWh. As the fuel cell efficiency decreases, more heat needs to be rejected by the cooling system. Due to the described degradation, the stack coolant outlet temperature at the highest current density of the polarization curve increases by 2.3 °C. The changes due to degradation have to be considered already during the design phase of a fuel cell system.

## 5. SUMMARY AND OUTLOOK

This publication shows the influence of degradation mechanisms on a fuel cell system at the test bed. Carbon corrosion is measured during start-up at a relatively constant level throughout the testing period. The cell voltages in a reference point and the deviation between the highest and lowest cell voltage in the stack are investigated. The results of several methods to evaluate membrane degradation show overall, that the membrane experiences thinning or even a starting pinhole formation. This is expressed by a reduced pressure resistance, a higher hydrogen concentration in the fuel cell exhaust and a faster voltage bleeding process. The differences of the polarization curves at BoT and EoT indicate a number of changes within the fuel cell, including a reduced catalytic activity and inhibited gas exchange. At EoT, an overall cell voltage degradation of 145  $\mu\text{V/h}$  or 12 mV/MWh is identified at high current densities.

## 6. REFERENCES

- [1] Pan M, Pan C, Li C et al. (2021) A review of membranes in proton exchange membrane fuel cells: Transport phenomena, performance and durability. *Renewable and Sustainable Energy Reviews* 141:110771. <https://doi.org/10.1016/j.rser.2021.110771>
- [2] Florian Poimer (2020) Methodology for Fuel Cell System Testing and Experimental Optimisation. Master Thesis, Graz University of Technology
- [3] Jouin M, Gouriveau R, Hissel D et al. (2016) Degradations analysis and aging modeling for health assessment and prognostics of PEMFC. *Reliability Engineering & System Safety* 148:78–95. <https://doi.org/10.1016/j.res.2015.12.003>
- [4] DOE, Fuel Cell Technologies Office (2011-2020) Multi-Year Research, Development, and Demonstration Plan
- [5] Kundu S, Fowler MW, Simon LC et al. (2006) Morphological features (defects) in fuel cell membrane electrode assemblies. *Journal of Power Sources* 157:650–656. <https://doi.org/10.1016/j.jpowsour.2005.12.027>
- [6] Linse N, Scherer GG, Wokaun A et al. (2012) Quantitative analysis of carbon corrosion during fuel cell start-up and shut-down by anode purging. *Journal of Power Sources* 219:240–248. <https://doi.org/10.1016/j.jpowsour.2012.07.037>
- [7] Cherevko S, Kulyk N, Mayrhofer KJJ (2016) Durability of platinum-based fuel cell electrocatalysts: Dissolution of bulk and nanoscale platinum. *Nano Energy* 29:275–298. <https://doi.org/10.1016/j.nanoen.2016.03.005>
- [8] Cheng X, Shi Z, Glass N et al. (2007) A review of PEM hydrogen fuel cell contamination: Impacts, mechanisms, and mitigation. *Journal of Power Sources* 165:739–756. <https://doi.org/10.1016/j.jpowsour.2006.12.012>
- [9] Bruijn FA de, Dam VAT, Janssen GJM (2008) Review: Durability and Degradation Issues of PEM Fuel Cell Components. *Fuel Cells* 8:3–22. <https://doi.org/10.1002/fuce.200700053>
- [10] Klell M, Eichlseder H, Trattner A (2018) Wasserstoff in der Fahrzeugtechnik. Springer Fachmedien Wiesbaden, Wiesbaden
- [11] Jonas K, Klingner M (2011) Alterung von Brennstoffzellen in Fahrzeugen – Prinzipien und Analysemethoden. *MTZ Motortech Z* 72:908–913. <https://doi.org/10.1365/s35146-011-0195-z>
- [12] Dubau L, Castanheira L, Maillard F et al. (2014) A review of PEM fuel cell durability: materials degradation, local heterogeneities of aging and possible mitigation strategies. *WIREs Energy Environ* 3:540–560. <https://doi.org/10.1002/wene.113>