# A1102

# Sensitivity analysis on the impact of air contaminants on automotive fuel cells

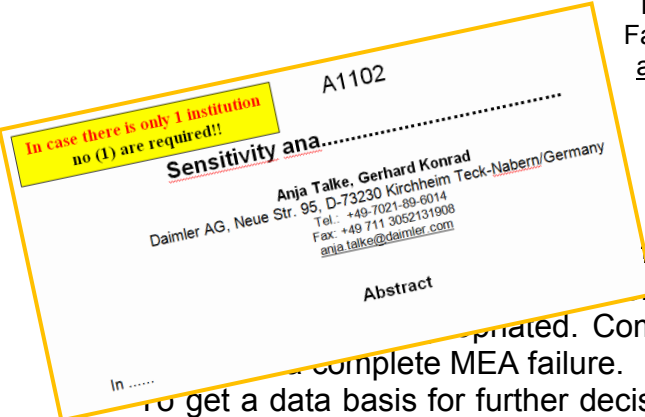**Anja Talke (1), Ulrich Misz (2), Gerhard Konrad (1), Angelika Heinzel (2)**
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## Abstract

arket introduction of series fuel-cell vehicles, detailed nal influences on the fuel cell, in particular the cathode phated. Common air contaminants cause power loss, decreasing complete MEA failure.

To get a data basis for further decisions in handling with noxious gases, the influences of air contaminants on PEMFC have been analysed extensively under automotive operating conditions systematically using a full factorial matrix test for the first time. The specific variation of temperature, voltage and harmful gas concentration resulted in 27 operating points for each used harmful gas.

First, the experiments were performed with a single cell, active area of 45.14 cm$^2$, straight flow channels and a loading of 0.4 mg cm$^{-2}$ Pt/C at the cathode. Subsequently, similar experiments were carried out with a ten-cell stack. This stack was different from the single cell due to a modified flow field, larger active area of 300 cm$^2$ and the gas distribution. Hence, it is closer to the real application.

The results generated with the single cell indicated significant degradation but as well the possibility of regeneration. The degradation caused by different harmful gases is both dependent on temperature and potential. The currently performed analysis with a stack shows differences in degradation behaviour in comparison to the single cell. These outcomes reveal the necessity of stack tests to provide application-oriented reliable results. The results give an overview of the cathode harming potential of the most relevant air contaminants, including an estimation of the degradation influence depending on the harmful gas concentration. Hence, the work provides a basis for the development of cathode air filter and regeneration techniques for automotive applications.
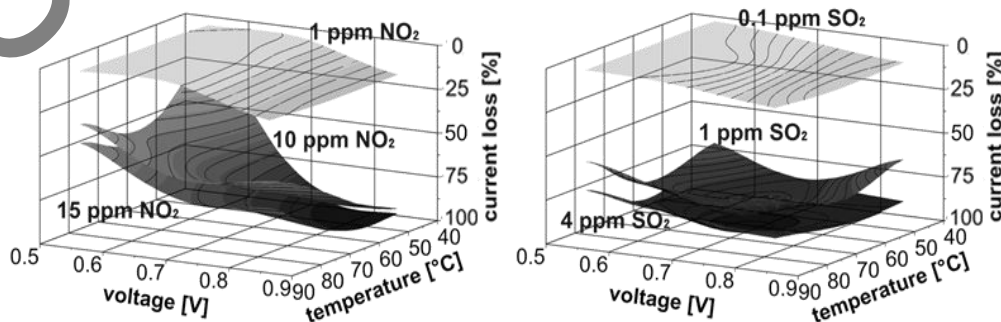
Figure 1: Current loss depending on voltage, temperature and concentration of contaminant (left: NO$_2$; right: SO$_2$)

# Introduction

Fuel cells are a promising technology to use renewable energy sources, both for stationary and mobile applications, especially in times of increasing concern for resource scarcity and climate change. For mobile applications the proton exchange membrane fuel cell (PEMFC) is the most promising option due to very dynamic operation and high efficiency even at low temperatures. Worldwide, already since the 80s concrete research and development take place in the automotive industry to launch a fuel cell-powered series vehicle on the market. Nevertheless there is no large series available until now. The reason is not the maturity of the technology, which is already fully developed. It is rather the high demands regarding the reliability, durability and not least the costs that are currently set for passenger cars. Thus, the automotive industry generally requires at least 6000 hours or 10 years lifetime for the main components. One factor that is known to reduce the lifetime is the negative influence of different air pollutants on the cathode of the fuel cell.

# 1. Scientific Approach

Negative influence of air pollutants is the subject of research for several years. The focus of published studies is mainly on common gaseous air pollutants such as sulphur compounds, nitrogen oxides, ammonia and some hydrocarbons. Sulphur dioxide ($SO_2$) is the most studied pollutant by far. This is due to the strong negative and often irreversible effects observed [4], [18], [2], [13], [14]. Mostly it is assumed that sulphur reacts directly with the platinum catalyst. This results in a decreased active catalyst surface, followed by a reduced or inhibited oxygen reduction reaction (ORR) [16], [17], [4], [14].

Other air pollutants are studied less extensively and especially exact reaction mechanisms are not known yet. Nitrogen oxides ($NO$, $NO_2$) show a strong negative but reversible effect in most studies [16], [15], [4], [12]. Toluene has a strongly negative impact already at low concentrations in the range of 100 ppb [9], [5], [6], [1]. The effect of ammonia ($NH_3$) is described differently [11], [8], [15], [3], [4]. Many studies show a weak and reversible degradation due to $NH_3$. Other publications observe a strong effect that moreover cannot be regenerated completely by using clean air at the cathode side.

It can be concluded that the results of some studies regarding the influence of air pollution on fuel cells differ strongly although the same noxious gases were investigated. A closer look reveals that on the one hand different equipment and different cell hardware was used. On the other hand, the operating conditions and the pollutant concentrations varied widely, which obviously has a large impact on the results.

The influence of the operating conditions is subject of a few publications. Thus, in [13] was studied the influence of current density on the effect of $SO_2$, for example. They could show that a higher current density increases the negative impact of $SO_2$. A variation of the temperature and of the voltage was carried out by [7]. They indicated that a high temperature tends to reduce the degradation caused by $SO_2$. But they also showed that a low voltage and accordingly high current density reduces the negative impact of $SO_2$, so they observed the opposite of [13].

Scientific literatures predicate an influence of operating conditions on the effect of air pollutants on the cathode. But the comparison above also illustrates that there is a lack of comparability in literature and the influence of operating conditions was not examined sufficiently until now. The present study therefore aims to systematically analyse the influence of the parameters temperature, voltage and pollutant concentration on the effect of selected air pollutants. For that purpose a full factorial experimental design was created.

# 2. Experiments

A first screening at potentially harmful gases should provide a broad overview of the effects of traffic related air pollutant on automotive fuel cells in dependence on the potential, temperature and concentration. Additionally differences between single cell operation with constant air flow and stack operation with adjusted cathode air supply were analysed.

Experiments at ZBT were conducted on hydrogen/ air PEM single cells employing hardware by Automotive Fuel Cell Cooperation – AFCC. This sub-scale test hardware was developed to assure good comparability to full-size hardware. It provides near-zero gradient conditions (iso-thermal, iso-baric, iso-potential) and for that reason simulates a section of a full-size hardware without critical undersupply. Furthermore the usage of this common test platform offers a huge database to compare and verify own measurements. The graphitic flow-field-plates have a parallel straight channel flow-field design and are therefore similar to full-size stack design. MEAs were also provided by AFCC with a loading of 0.4 mg cm$^{-2}$ Pt/C on the cathode; 0.1 mg cm$^{-2}$ Pt/C + RuO$_2$ on the anode. Membranes consisted of a perfluorinated polymer similar to Nafion with 18μm. The active area of the catalyst layer was 48.5 cm$^2$ and a clamping pressure of 6 bar$_{rel}$ was used. A test bench was adapted for the harmful gas screenings. At ZBT all tests of the harmful gas screenings were performed at 100 % humidification at anode and cathode side. The test bench construction is shown in Figure 2.
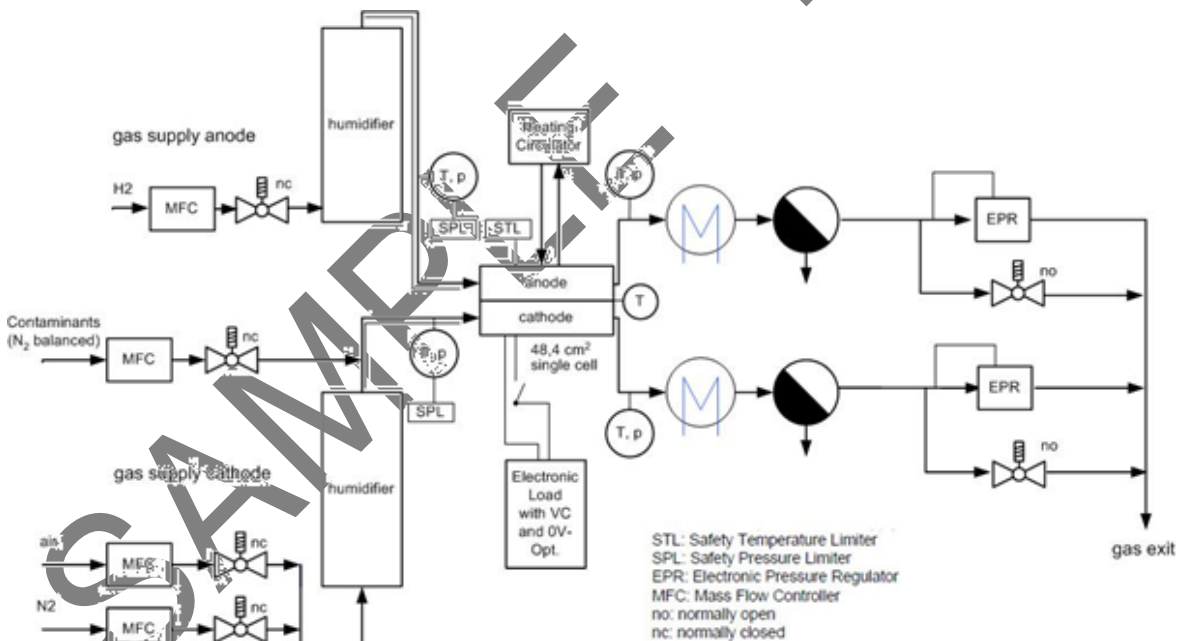


Figure 2: schematic diagram of the single cell test stand at ZBT

Humidification was done using bubble humidifiers with automated water replenishment. To reduce the accumulation of impurities in the humidifier, deionized water was continuously drained slightly at the bottom of the bubble humidifiers. This procedure ensured a permanent water exchange. The feed gases were supplied with high stoichiometry to prevent undersupply at each operating point. A pressure control of the company Alicat Scientific® was installed behind the stack to adjust automotive test conditions with a

constant absolute pressure. To protect the controllers against moisture, the downstream exit gases were cooled by heat exchangers and the condensate was deposited by condensation separators. By using constant flow rates of 12 L min$^{-1}$ pressure air at cathode side and 2 L min$^{-1}$ hydrogen at anode side no pressure fluctuations had to be corrected. The pressure drop across the cathode flow field was about 580 mbar and was taken into account accordingly. The overpressure was 1.5 bar$_g$ at cathode and 1.7 bar$_g$ at anode.

**Experimental differences between single cell and stack tests**

To analyse the short stacks an additional test bench was built at Daimler. In contrast to the work performed at ZBT, the fuel cell stack experiments at Daimler were conducted with membrane humidifiers using deionized water in counterflow to provide 80% relative humidity. The stoichiometry was set between 1.65-16 for both anode and cathode. Besides that variable pressures (1.1 - 2.9 bar$_{abs}$) and flow rates between 0.027 – 0.648 L min$^{-1}$ on anode side and 7.2 – 288 L min$^{-1}$ on cathode side were used. In order to create automotive conditions the flow rates were controlled by the resulting current, i.e. only the needed amount of gas for a specific load point was fed in. At Daimler a larger ten-cell short stack designed for automotive applications by AFCC was used. MEAs had a loading of 0.4 mg cm$^{-2}$ Pt/C on cathode; 0.1 mg cm$^{-2}$ Pt/C + RuIrOx OER (Oxygen Evolution Reaction) catalyst on the anode. Membranes consisted of reinforced Poly-Tetra-Fluor-Ethylene based material with 18 μm. The active area of the catalyst layer was 300 cm$^2$ and a straight flow-field was used. Therefore the experimental design had to be modified slightly to meet the requirements for this hardware.

The test procedure was designed with Daimler and automated implemented at ZBT test bench for the single cell analyses. The total experimental procedure is explained in the following section. For each contaminant a new MEA was used. Before starting the screening, the MEA was conditioned for 12 hours at a cell temperature of 60°C and a current density of 1 A cm$^{-2}$. Subsequently, a current-voltage characteristic at the selected power points between 0 and 2.5 A cm$^{-2}$ was recorded to characterize the MEA performance. In order to investigate the influence of pollutants under different conditions systematically, a full factorial design for the experiments was set up. This procedure should ensure that the effects of the pollutant, pollutant concentration, temperature and the potential could be separated and assessed as precise as possible. The tests were also carried out with a constant voltage, since it is known from literature that, in many cases, the potential exerts an influence on the reaction of the pollutant in the cell. In current-controlled tests the voltage varies in a wide range and thus various uncontrollable reactions of pollutants occur. In order to get reliable results, a matrix of 3 different contaminant concentrations, 3 different temperatures and 3 different potentials were used. The test-matrix therefore consisted of 3 x 3 x 3 = 27 operating points with a total measurement time of eight days for each contaminant. The operating points have been selected in order to reflect realistic ranges of operation in vehicles. Within the 27 operating points, respectively, the same measurement procedure was performed (Figure 3):

1) The cell was conditioned under the respective conditions for one hour to ensure a constant operation.
2) The cell was exposed for one hour to the selected contaminant concentration
3) The cell was operated for one hour with clean air to analyse the reversibility of the pollutant effect without further procedures like potential cycling.
4) Cleaning cyclic voltammetry (CV) measurements were performed to study the regeneration at high voltages up to 1 V.

5) Regular assessment points (RAP) were recorded.

The record of 4 characteristic points (RAP) was chosen to represent the different areas of the current-voltage-characteristic. Especially the voltage, which is measured at 0.1 A cm$^{-2}$, shows the effect on the catalyst, because only the kinetic losses occur at this point. Thus a comparison with the reference measurement can provide information about the degradation of the catalyst area. The RAP were performed after CV recovery, so they are generally suitable to demonstrate the reversibility of the effect of contaminants.
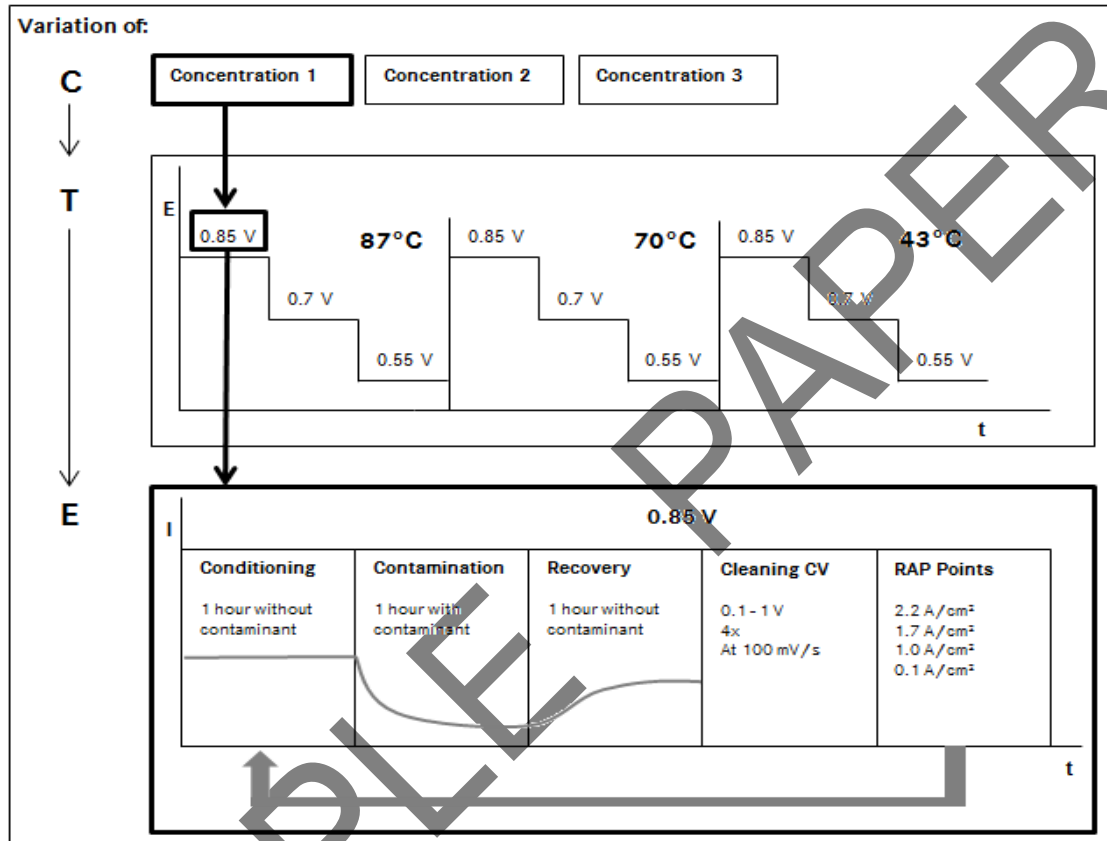


Figure 3: Experimental procedure single cell - full factorial matrix screening

**Screening procedure differences between single cell and stack tests**
The experimental design at Daimler was slightly modified as well to meet the requirements for the short stack. The highest voltage was reduced to 0.8 V instead of 0.85 V. The highest temperature was reduced to 80°C instead of 87°C. Instead of CV-measurements a specific cleaning procedure was used to achieve regeneration of the cells. One short stack was used for all experiments with NO and NO₂.

# 3. Results

The present paper shows the first results of a broad measurement matrix. The investigations are part of a large project called ALASKA, that runs until early 2017. The main topic in this paper is the comparison between single cell and stack operation and the resulting effects of harmful gases in air on the cell. First of all the effects of nitrogen oxide (NO) and nitrogen dioxide (NO₂) were analysed. These two air contaminants reach peak concentrations up to 2 ppm and higher [10], especially at rush hour traffic, behind buses and trucks and in tunnels, where photochemical reactions due to lack of exposure to sunlight do not occur.

**Single fuel cell**

The harmful concentrations being used in the analysis with the single cell were 1, 10 and 40 ppm NO and 1, 10 and 15 ppm $NO_2$.

Both NO and $NO_2$ indicated similar behaviour with a strong current loss in the single cell directly from the start of the injection. The gases showed an effect starting at a concentration of 1 ppm, but only at the lowest temperature range of 43°C. Almost all experiments exhibited an asymptotic behaviour of the current, which dropped off sharply at the beginning and approached a limit region after some time. The asymptotic behaviour caused that most of the current loss occurred in the first few minutes. Both gases led to a current decrease up to 10% already at 1ppm.

10 ppm NO showed a current reduction between 50% and 80%, whereas $NO_2$ caused a slightly weaker current loss of 35% within the first minutes and up to 70% after one hour poisoning. The highest concentration of 15ppm $NO_2$ led to current declines of 50% up to 80%. During supply of 40 ppm NO in air, which is significantly higher than any other pollutant concentration used at the screening, current reductions between 60% and almost 90% were observed. These cases already evidenced that there is no linear relationship between concentration and current loss.

Regeneration processes showed the same asymptotic behaviour. Firstly a very rapid recovery of the current took place and flattened significantly towards the end. At least half of the current can be recovered for both gases within one hour, often even considerably more.

With respect to the influencing factors, a slight correlation with temperature was observed. Lower temperatures tended to increased degradation, followed by slower regeneration. A correlation between cathode potential and $NO_x$ effects could not be observed. However, the analysis revealed that the degree of regeneration is almost determined exclusively by the temperature and less by the pollutant concentration. The higher the temperature, the faster and more complete regeneration took place for both NO and $NO_2$.

**Short fuel cell stack**

Concentrations up to 10 ppm were supplied to the air stream at cathode side of the PEFC short stack. First of all it is important to mention that due to the different operating conditions especially the stoichiometry on the cathode site, the single cell was exposed to a much higher amount of noxious gases in comparison to the short stack, based on cm² active area (Table 1). Therefore, it was assumed that the negative effects will not be as severe in the stack as in the single cell.

However, in comparison with the measurements at the single cell the short stack showed a higher sensitivity, especially at low concentrations of 1 ppm NO (Figure 4). While the current of the single cell lost 5 - 10 % of its initial value at the end of the pollutant injection phase, the short stack experiments revealed a stronger current loss of about 15 % of the initial value. This is especially noticeable because of the lower amount of the supplied pollutant per active cell area at the short stack. The ability for regeneration with clean air supply was very low in the measurements with 1ppm. After one hour the current did not reach the initial value in any measurement, losses remained up to 8%.

The experiments with 10 ppm NO at the short stack also exhibited an asymptotic behaviour of the current with a strong power loss during the first minutes. After one hour the current decreased to approximately 30% of the initial value. In the measurements with 10 ppm the single cell shows a slightly higher sensitivity with a current loss of 70 - 80% after one hour.
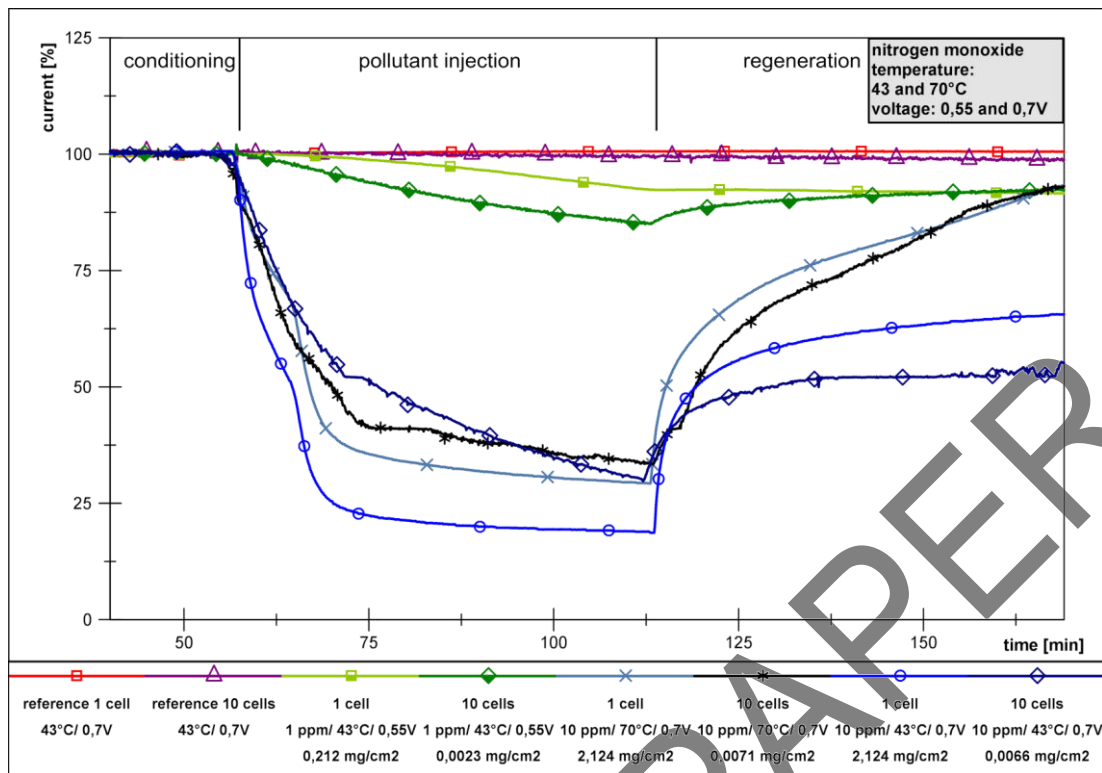
Figure 4: Comparison of tests with single cell/ ten cell short stack. Pollutant: nitrogen monoxide 1 and 10 ppm at 43 and 70 °C/ 0.55 and 0.7V. Current in %.

This higher loss was due to the much higher quantity of pollutant resulting from the increased stoichiometry in the single cell. The amount of the supplied NO per active cell area in the short stack experiments was only 0.3% of the applied amount in the single cell. Despite large differences in the amount of supplied NO and the slight differences in exposure time on single cell and stack, the differences in current loss were quite low (Table 1).

Table 1: Comparison between single cell and short stack regarding current loss, mass of pollutant and exposure time

| cells | conditions | current [%] after pollutant injection | current [%] after regeneration | mass of pollutant [mg/cm²] | exposure time [ms/cm²] |
|-------|-----------|---------------------------------------|--------------------------------|----------------------------|------------------------|
| 1 | 1ppm NO/ 43°C/ 0,55V | 92,5 | 91,6 | 0,212 | 0,098 |
| 10 | 1ppm NO/ 43°C/ 0,55V | 85,3 | 92,5 | 0,002 | 0,014 |
| 1 | 10ppm NO/ 43°C/ 0,7V | 18,7 | 65,4 | 2,124 | 0,098 |
| 10 | 10ppm NO/ 43°C/ 0,7V | 30,4 | 53,4 | 0,007 | 0,037 |
| 1 | 10ppm NO/ 70°C/ 0,7V | 29,3 | 92,7 | 2,124 | 0,076 |
| 10 | 10ppm NO/ 70°C/ 0,7V | 33,6 | 95 | 0,007 | 0,018 |

The regenerative capacity was relatively high and temperature dependent also in the short stack tests. At 43°C the current reached 53 % of the initial value after one hour with clean air, while at 70°C regeneration up to 95 % of the initial value was possible.

The significantly more sensitive behaviour of the short stacks in comparison to the single cell can be explained by the differences in test bench/ test procedure. The amount of gas supplied in the short stack test bench as well as in a fuel cell vehicle was set via the current. If the current decreases also the amount of supplied gas decreases as can be seen in Figure 4.
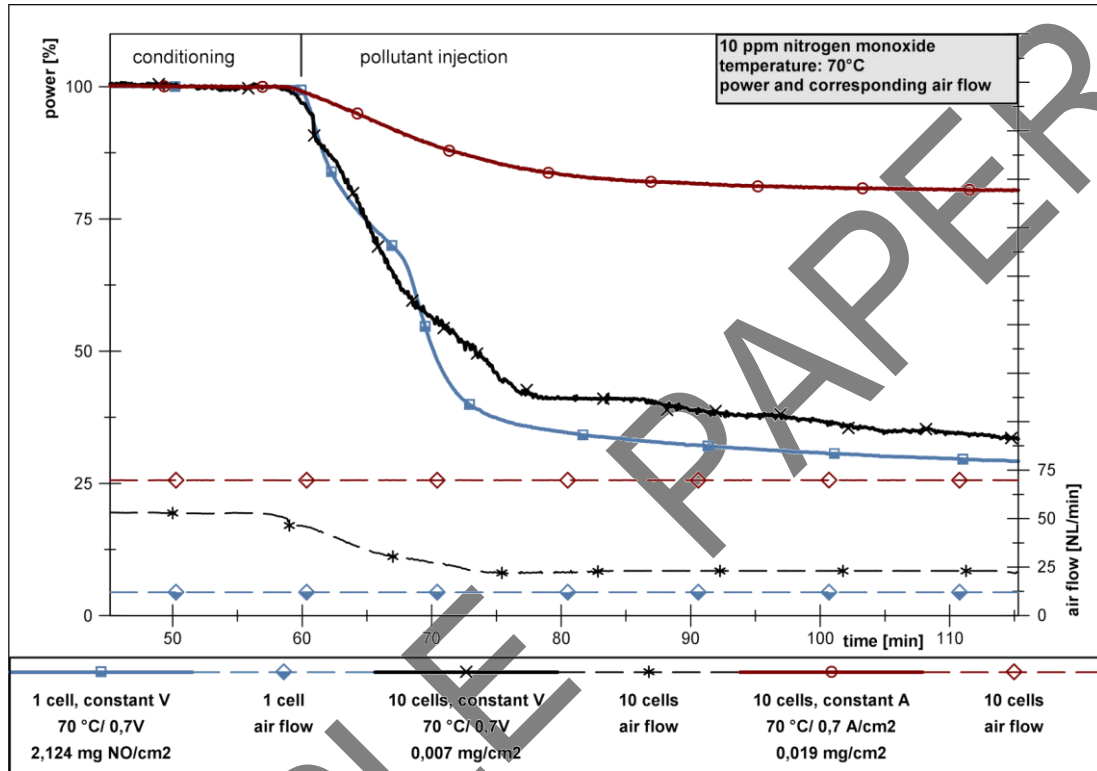


Figure 4: Comparison of percentage power losses and air flow rates of 3 different experimental designs

The amount of gas supplied in the single cell test bench was kept constant, however, as these test benches were designed to represent a well-supplied central cell of a full scale stack and therefore under-supply was to be avoided at any time. In experiments carried with constant voltage in case of a power reduction of the cell by pollutants the current decreased whereby at the same time the amount of gas supplied was reduced. For a previously damaged fuel cell, in which ECSA was reduced or diffusion processes were disturbed this resulted in a further deterioration causing an increased sensitivity of the stack to pollutants. This behaviour was due to the control of the gas supply and could not be observed in tests with constant current. Figure 4 shows a comparison of three different experiments and the associated air streams. Two experiments were carried out with constant voltage, one at a single cell and one at a short stack. The third experiment was run with constant current at a short stack. For the comparison of the experiments the graphs are shown as percentage power. If the injected amount of pollutant was considered, the short stack with constant voltage showed the most sensitive behaviour due to the reduced gas flow. For real application in the vehicle, such attitudes are still relevant. When the power of the stack is decreased, for example due to the impact of pollutants, the lower voltage limit will be attained in load points with high current consumption. In this case, the current will be reduced to ensure meeting of the voltage

limit. At the same time, the gas supply is also decreased which results in an increased sensitivity of the fuel cell stack towards air pollutants.

## 4. Conclusions

The present paper shows the first results of a large project, called ALASKA which deals with measurements of real occurring pollutant concentrations at traffic related areas, analysing the effects of these pollutants on fuel cells under automotive conditions, developing regeneration strategies of the stacks and finally designing new cathode air filters.

The harmful gas screenings at the single cell and short stacks show the influence of operating conditions on the degrading effect of the pollutants. The first analyses were carried out with NO and $NO_2$. The following results could be determined:

- NO and $NO_2$ lead to a current drop even at concentrations of 1 ppm
- A correlation with temperature was observed, both in degradation and in the subsequent regeneration of single cell and short stack
- The higher the temperature, the faster and more complete regeneration took place for both NO and $NO_2$
- There is no linear link between power loss and pollutant concentration
- The comparison of the measurements with a short stack exhibited its higher sensitivity for air pollutants in contrast to the single cell. This behaviour is caused by the simultaneous reduction of the gas supply with current decline at stack operation compared with the constant gas supply at single cell operation.

The first results demonstrate the importance of performing pollutant gas analysis under automotive operating conditions. Tests with individual cells are suitable to analyse the damage mechanisms of different pollutants on the MEA, particularly with the aid of electrochemical measurement methods. In addition, the need for realistic tests on short stacks was demonstrated to assess the actual relevance of the topic for fuel cell vehicles.

The sensitivity of the short stacks at Daimler test bench is also to be expected at the high load points in a fuel cell vehicle. Within this project period, the target is to get a complete overview of the effects of traffic related air pollutants on fuel cells under automotive operating conditions.

## Acknowledgements

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