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Impact of Air Contaminants on Subscale Single Fuel Cells and an Automotive Short Stack

Anja Talke[1], Ulrich Misz[2], Gerhard Konrad[1] and Angelika Heinzel[2]

1. Daimler AG, Neue Str. 95, Kirchheim/Teck-Nabern D-73230, Germany

2. ZBT GmbH, Carl-Benz-Str. 201, Duisburg D-47057, Germany

Abstract: In order to achieve a successful market introduction of series fuel-cell vehicles, detailed knowledge about the impact of external influences on the fuel cell, in particular the cathode catalyst must be appropriated. Common air contaminants cause power loss, decreasing lifetime or a complete MEA (membrane electrode assembly) failure. To get a data basis for further decisions in handling with noxious gases, the influences of air contaminants on PEMFC (proton exchange membrane fuel cell) have been analyzed extensively under automotive operating conditions using a subscale single cell and a full scale short stack. 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 cathode side. 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 currently performed analyzes with a short stack shows differences in degradation behavior in comparison to the single cell. In general the single cell showed a higher sensitivity to air pollutants mainly due to a higher mass of injected pollutant. But in case of constant voltage mode the short stack exhibited an increased sensitivity because of the specific control of the test bench. These outcomes reveal the necessity of stack tests to provide application-oriented reliable results.

Key words: Fuel cell, air contaminants, NOx, automotive applications, short stack, PEMFC.

1. 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 PEMFC (proton exchange membrane fuel cell) is the most promising option due to very dynamic operation and high efficiency even at low temperatures. Worldwide, already since the 80s sizeable research and development took 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 last but not least the costs that are currently set for passenger cars. Thus, the automotive industry generally requires at least 5,000 hours or 10 years lifetime for the main components [1]. One factor that is known to reduce the lifetime is the negative influence of different air pollutants on the cathode of the fuel cell [2].

Corresponding author: Anja Talke, M. Eng., research fields: automotive fuel cells and systems and system compounds.

2. Scientific Approach

Negative influence of air pollutants is the subject of research since several years. The focus of published studies is mainly on common gaseous air pollutants such as sulfur compounds, nitrogen oxides, ammonia and some hydrocarbons. SO_2 (sulfur dioxide) is by far the most studied pollutant. This is due to the strong negative and often irreversible effects observed [3-7]. Mostly it is assumed that sulfur reacts directly with the platinum catalyst. This results in a decreased active catalyst surface followed by a reduced or

inhibited ORR (oxygen reduction reaction) [3, 7-9].

Other air pollutants are studied less extensively and often exact reaction mechanisms are not known yet. Nitrogen oxides (NO, NO_2) show a strong negative but reversible effect in most studies [3, 8, 10, 11]. St. Pierre et al. [11] assumed that nitric oxides in general adsorb mostly as NO on platinum in the potential range of a PEMFC. In Ref. [12] it is shown that there are different forms of adsorption on platinum like linearly or bridge bonded NO covering different numbers of platinum sites. Depending on the potential NO further gets reduced or oxidized to different products like nitrogen, nitrite or ammonium for example [11]. Based on their model for NO_2 contamination they predict an acceptable concentration of 0.39 ppm NO_2 in the air feed over lifetime for automobile applications. The maximum allowable short term concentration should not exceed 0.9 ppm NO_2 to avoid system failure. The annual average of NO_2 in Germany 2014 was only 0.005-0.024 ppm [13]. Considering a fuel cell car moving between cars with combustion engines the expectable concentrations are most likely higher. Especially peak concentrations in cities and tunnels can easily exceed 2 ppm NO_x [14]. This clearly shows the relevance of further investigation of the influence of nitric oxides on fuel cells to develop suitable remedies.

Moreover almost all studies published so far were conducted on subscale test hardware. Single cells with a small active area as well as non-automotive operating conditions were used. This is necessary for fundamental analyses of the reaction mechanisms of the pollutants. However, this is not suitable for the development of applicable remedies such as an activated carbon air filter. But remedies might be required for mobile applications especially because of reduced platinum loadings for future applications which lead to higher sensitivity of fuel cells.

The present study therefore aims to systematically analyze the differences of the effect of air pollutants on subscale single cells and full scale short stacks. Two different test benches were used and the operating conditions were selected to be in the range of conditions used in fuel cell vehicles.

3. Experiments

Experiments at ZBT were conducted on hydrogen/air PEM single cells employing hardware by AFCC (Automotive Fuel Cell Cooperation). This sub-scale test hardware was developed to assure good comparability to full-size hardware. It provides near-zero gradients 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 the full-size stack design. MEAs were also provided by AFCC with a loading of 0.4 mg cm^{-2} Pt/C on the cathode and 0.1 mg cm^{-2} Pt/C + RuO_2 on the anode. Membranes consisted of a perfluorinated polymer similar to Nafion® with a thickness of 18 µm. The active area of the catalyst layer was 48.5 cm^2 and a clamping pressure of 6 bar_g was used. A test bench was adapted for the measurements using different harmful gases in air as pollutants. At ZBT all tests of the measurement campaign were performed at 100% humidification at anode and cathode side. The test bench construction is shown in Fig. 1.

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

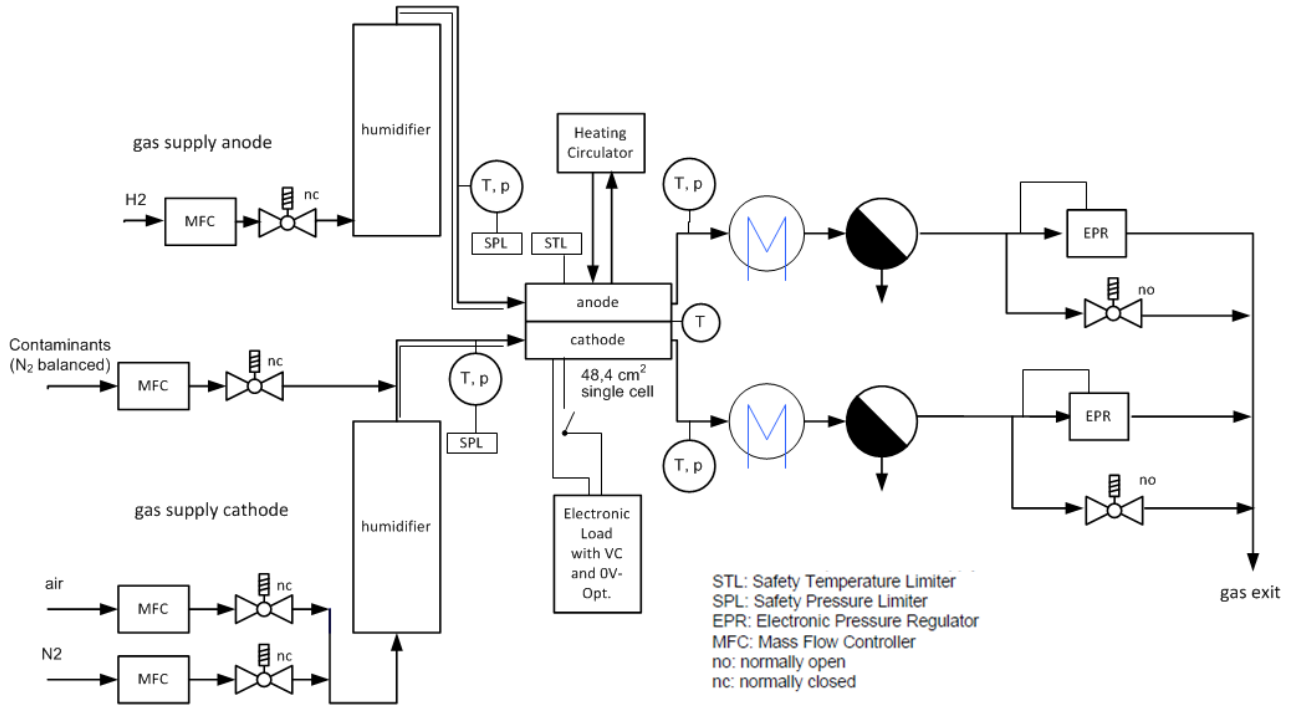

Fig. 1 Schematic diagram of the single cell test stand at ZBT.

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 on the cathode side and 1.7 bar_g on the anode side.

3.1 Experimental Differences between Single Cell and Stack Tests

To analyze the short stacks an additional test bench was built at Daimler AG. In contrast to the work performed at ZBT, the fuel cell stack experiments at Daimler AG were conducted with membrane humidifiers using deionized water in counter flow 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 AG 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 and 0.1 mg cm^{-2} Pt/C + RuIrOx catalyst on the anode. Membranes consisted of reinforced Poly-Tetra-Fluor-Ethylene based material with 18 µm thickness. 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 bench construction is shown in Fig. 2.

The test procedure was designed with Daimler AG and automated at ZBT test bench for the single cell analyzes for comparability reasons. For each contaminant a new MEA was used. Before starting the test, 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 selected current points between 0 and 2.5 A cm^{-2} was

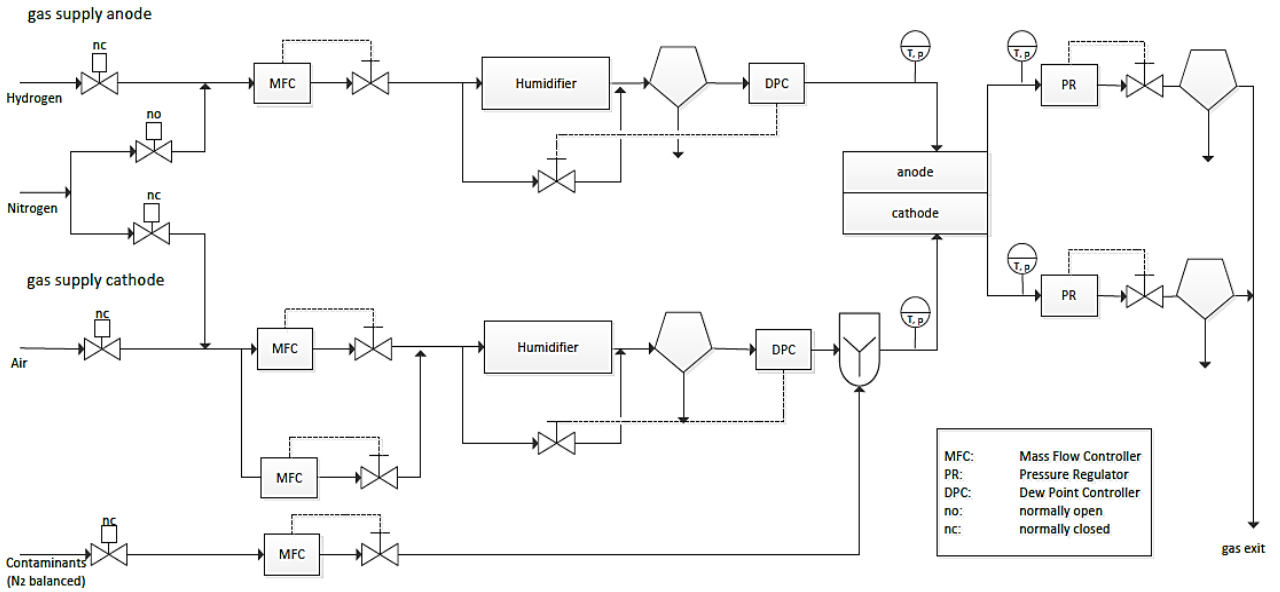

Fig. 2 Schematic diagram of the short stack test stand at Daimler AG.

recorded to characterize the MEA performance. In order to investigate the influence of selected air pollutants systematically the pollutant concentration, temperature and the potential was varied. The operating points have been selected in order to reflect realistic ranges of operation in vehicles. Therefore temperatures of 43, 70, 87 °C and potentials of 0.55, 0.7, 0.85 V have been chosen. At ZBT the tests were solely carried out with a constant voltage, since it is known from literature that in many cases the potential influences 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 the pollutants occur. The resulting test procedure was set as follows:

(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 analyze the reversibility of the pollutant effect without further procedures like potential cycling;

(4) Cleaning CV (cyclic voltammetry) measurements were performed to study the regeneration at high voltages up to 1 V;

(5) RAPs (regular assessment points) were recorded.

The recording 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 RAPs were performed after CV recovery, so they are generally suitable to demonstrate the reversibility of the effect of contaminants.

3.2 Differences between Single Cell and Stack Test Benches

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 NO_2.

4. Results

The investigations are part of a large BMWi funded 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 NO (nitrogen oxide) and NO_2 (nitrogen dioxide) were analyzed. These two air contaminants reach peak concentrations up to 2 ppm and higher [12], especially at rush hour traffic, behind buses and trucks and in tunnels, where photochemical decomposition reactions due to a lack of exposure to sunlight do not occur.

4.1 Single Fuel Cell

The concentrations of harmful gases in air being used in the analysis with the single cell were 1, 10 and 40 ppm NO and 1, 10 and 15 ppm NO_2. All tests were conducted at constant voltage.

Both NO and NO_2 indicated a strong current loss in the single cell directly after the start of the injection. The gases showed an effect already at a concentration of 1 ppm. Experiments exhibited an asymptotic behavior of the current, which dropped off sharply at the beginning and approached a limit region after some time. The asymptotic behavior caused that most of the current loss occurred in the first few minutes. Both gases led to a current decrease of 30% on average and up to 65% at 1 ppm.

10 ppm NO showed a current reduction between 40% and over 90% after one hour of poisoning. The highest concentration of 15 ppm 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 40% and over 90% were observed. These test-cases already prove that there is no linear relationship between concentration and current loss over time.

Regeneration processes showed an analogous asymptotic behavior. 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 exclusively determined 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.

4.2 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 the different operating conditions especially the stoichiometry on the cathode site. Consequently the single cell was exposed to a much higher amount of noxious gases in comparison to the short stack, based on cm^2 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.

In fact, within tests with constant current the short stack showed a lower sensitivity especially at low concentrations of 1 ppm NO. For the short stack hardly any effect could be observed while the single cell already lost about 28% of its power at 70 °C and 0.7 V (Fig. 3). Experiments with 10 ppm NO revealed a similar behavior. The short stack loses about 20% of its power at 70 °C and 0.7 A, which is even less than the effect of 1 ppm on the single cell (Fig. 3). With 10 ppm NO in air supply at 70 °C and 0.7 V the single cell loses about 70% of its power. As mentioned before this behavior is clearly due to the very high mass of pollutant per active area in the single cell in comparison to the short stack. In these experiments the

Table 1 Comparison between single cell and short stack at constant voltage regarding current loss, mass of pollutant and exposure time.

Cells	Conditions	Current [%] after pollutant injection	Current [%] after regeneration	Mass of pollutant [mg cm^{-2}]	Exposure time [ms cm^{-2}]
1	1 ppm NO/43°C/0.55V	72.5	85.5	0.212	0.098
10	1 ppm NO/43°C/ 0.55V	85.3	92.5	0.002	0.014
1	10 ppm NO/43°C/0.7V	18.4	61.2	2.124	0.098
10	10 ppm NO/43°C/0.7V	30.4	53.4	0.007	0.037
1	10 ppm NO/70°C/0.7V	28.2	89	2.124	0.076
10	10 ppm NO/70°C/0.7V	33.6	95	0.007	0.018

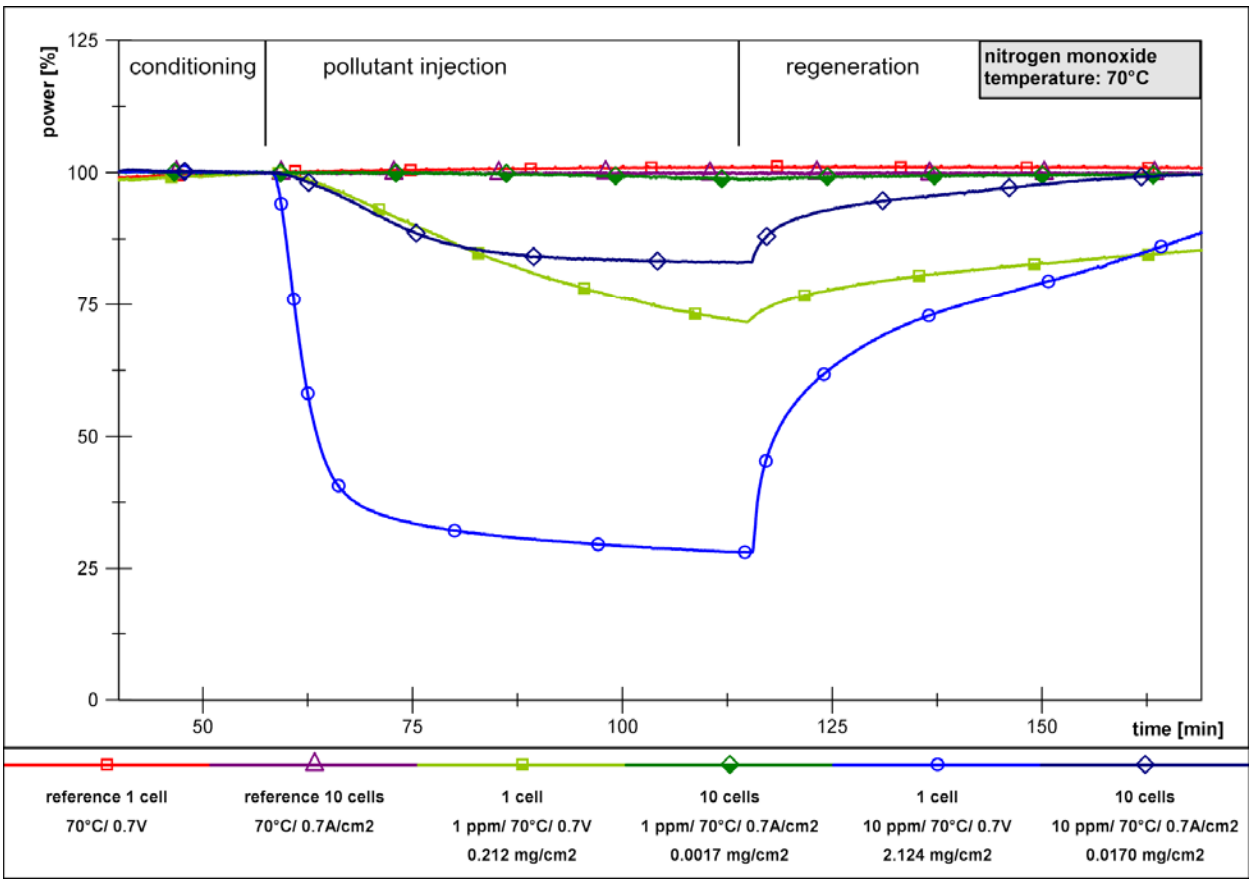

Fig. 3 Comparison of tests with single cell at constant voltage/ten cell short stack at constant current. Pollutant: nitrogen monoxide 1 and 10 ppm at 70 °C and 0.7 V. Power in %.

mass of pollutant used in the single cell was about 124 times the mass used in the short stack (Fig. 3).

However, within the experiments with constant voltage the short stack revealed a much higher sensitivity with power losses similar to the single cell. During the injection of 1 ppm NO at 43 °C and 0.55 V the short stack lost about 15% of its initial current while the single cell lost about 25% (Fig. 4). This is especially noticeable because 1 ppm NO did not have an effect on the short stack in the experiments with constant current although the mass of injected pollutant was comparable (1.7 µg cm^{-2} at constant voltage/2.3 µg cm^{-2} at constant current). The mass of NO injected in the single cell added up to 212 µg cm^{-2}.

The ability for regeneration with clean air supply was very low in the measurements with 1 ppm. After one hour the current did not reach the initial value in

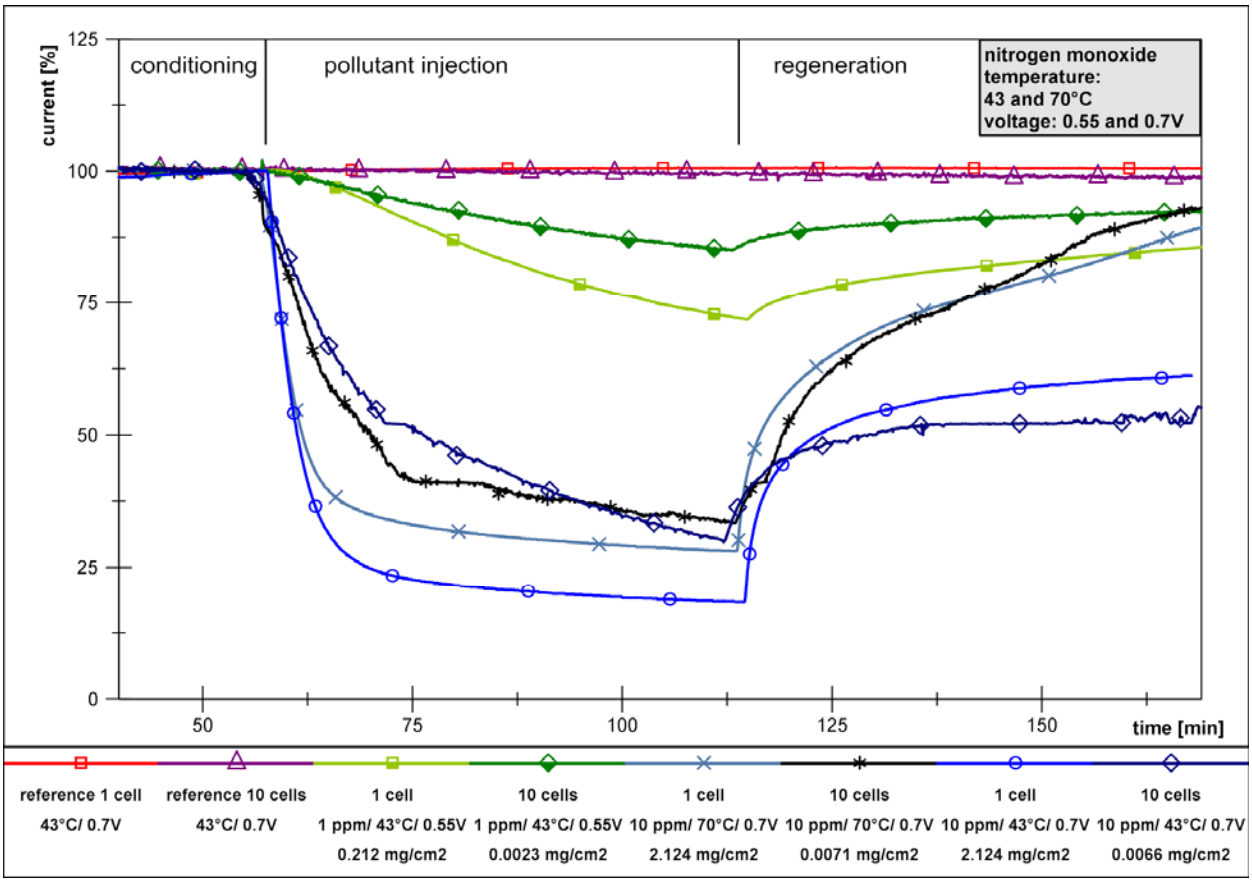

Fig. 4 Comparison of tests at constant voltage with single cell/ten cell short stack. Pollutant: nitrogen monoxide 1 and 10 ppm at 43 and 70 °C/0.55 and 0.7 V. Current in %.

any measurement, losses remained up to 8%.

The experiments with 10 ppm NO at the short stack also exhibited an asymptotic behavior of the current with a strong power loss during the first minutes. After one hour the current decreased to about 70% of the initial value. In the measurements with 10 ppm the single cell also showed a slightly higher sensitivity with a current loss of 70-80% after one hour.

Despite large differences in the amount of supplied NO and only slight differences in exposure time of the gases on single cell and stack, the differences in current loss were quite low (Table 1). The exposure time was calculated by the integration of the areas of the flow field channels. These values were compared to the actual gas flow to verify if there are significant differences due to the different design of the fuel cell hardware. The calculated values in ms cm^{-2} are shown in Table 1.

The recoverability of the performance loss was quite high and temperature dependent in the short stack tests, too. 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 behavior of the short stacks in the experiments with constant voltage can be explained by the differences in the test benches and the 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. These effects can be seen in Fig. 5.

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 cell of a full scale stack and therefore under-supply was

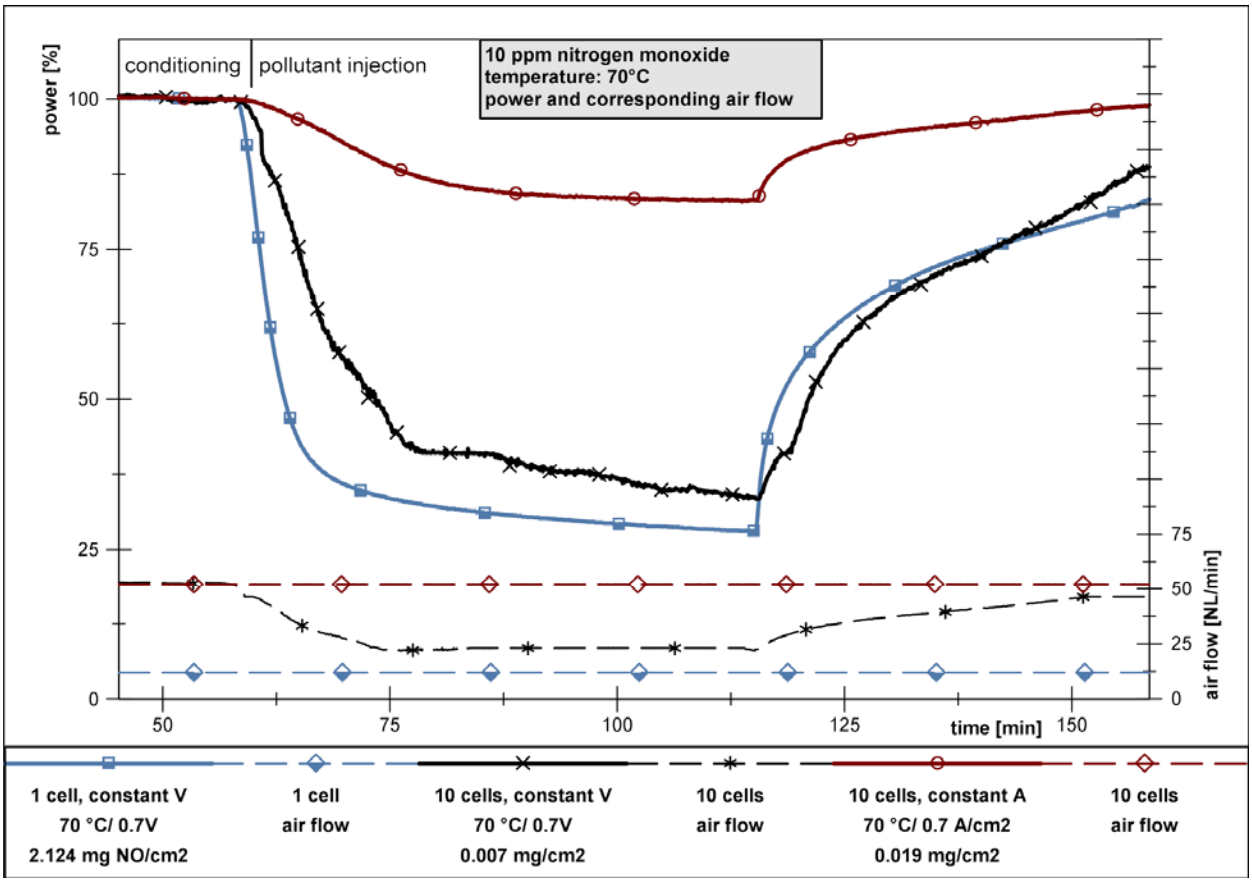

Fig. 5 Comparison of percentage power losses and air flow rates of 3 different experimental designs.

to be avoided at any time. In experiments carried out with constant voltage in case of a power reduction of the cell the current decreased. Therefore the amount of supplied air and hydrogen was reduced as well. For a previously damaged fuel cell, in which ECSA was reduced or diffusion processes were disturbed, this resulted in a further deterioration. This further deterioration is causing an increased sensitivity of the stack to pollutants. This behavior was due to the control of the gas supply and could not be observed in tests with constant current. Fig. 5 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 behavior 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.

5. Conclusions

The present paper shows the first results of the BMWi funded project ALASKA which deals with measurements of real occurring pollutant concentrations at traffic related areas, analyzing the effects of these pollutants on fuel cells under automotive conditions, developing regeneration strategies of the stacks and finally designing novel

cathode air filters.

The first experiments with the single cell and short stacks were carried out with NO and NO_2. The following results could be determined:

(1) NO and NO_2 lead to a current drop even at concentrations of 1 ppm;

(2) A correlation with temperature was observed, both in degradation and in the subsequent regeneration of single cell and short stack;

(3) The higher the temperature, the faster and more complete regeneration took place for both NO and NO_2;

(4) There is no linear link between power loss and pollutant concentration;

(5) The comparison of the measurements with a short stack exhibited its high sensitivity for air pollutants in some operating points. This behavior 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 analyze 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. The overview is the basis for the development of suitable air filter. Current air filters are able to filter NO_x, but they need to be adjusted with respect to pressure loss, break through behavior and packaging.

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