Influence of urban air on proton exchange membrane fuel cell vehicles – Long term effects of air contaminants in an authentic driving cycle

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HIGHLIGHTS

- PEMFC stack tests with NO, NO_2, SO_2, NH_3 and a driving profile from a street course.
- Accompanying online measurements of contaminant concentrations on the street course.
- Power losses from 5% to 10% by nitrogen oxides expected for FC-vehicles in Germany.
- NH_3 leads to power losses of < 3% but causes a progressive irreversible damage.
- Study reveals a significant negative influence of air pollutants on FC-vehicles.

GRAPHICAL ABSTRACT
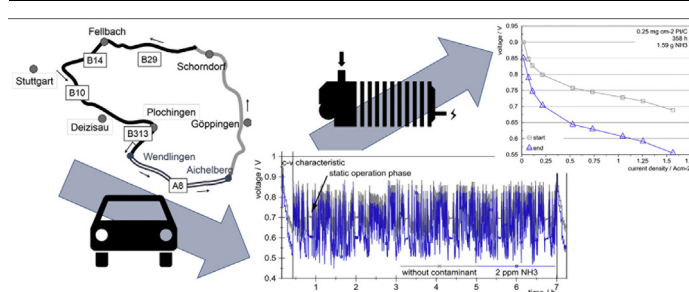
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ABSTRACT

Traffic related air pollutants cause power losses and decrease the lifetime of proton exchange membrane fuel cell (PEMFC). The relevance of this influence for vehicles is not exactly known due to a lack of studies under realistic conditions. Therefore, the present study aims at a better understanding. For the first time ever the influence of selected air pollutants on automobile fuel cell short stacks with different platinum loadings and a realistic driving cycle is examined. The driving cycle used, is an existing course near the city of Stuttgart, Germany. The experiments were accompanied with online measurements of relevant contaminant concentrations on the course. Furthermore, tests with a semi-dynamic profile have been executed for more than 1500 h and show an irreversible damage of the PEMFC by nitrogen oxides. With respect to the present results, spontaneous power losses of about 5% and over 10% in special situations by the nitrogen oxides can be expected for fuel cell vehicles in urban areas. NH_3 will lead to a spontaneous power loss of less than 3%, but causes a progressive irreversible damage. Together the tests reveal that air pollutants have a significant negative influence on fuel cell vehicles in urban areas.

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1. Introduction

With regard to climate protection and the protection of the population against pollutants, electro mobility is becoming increasingly important worldwide. PEMFC can play a key role since they combine high driving ranges with short refueling times. However, the costs of the fuel cell systems have to be further reduced and the durability of the systems must be further increased. Particularly in the context of the durability of the system, it is known that several air pollutants lead to a short-term loss of power and reduce the lifetime of fuel cells in the long term. This negative influence of air pollutants has been the subject of research for several years. The focus of available studies has mainly been on the reaction mechanisms of common gaseous air pollutants such as sulphur components, nitrogen oxides, ammonia and some hydrocarbons. Anyhow, most of these studies were conducted on subscale test hardware. Single cells with a small active area as well as non-automobile operating conditions were used. This is necessary for the fundamental analysis of the reaction mechanisms of the air pollutants but it is not suitable in order to discover the relevance of the influence of these components on fuel cell vehicles in urban areas. Beyond that, due to the reduced platinum loadings for future applications, a higher sensitivity of fuel cells towards air contaminants is predicted and needs to be examined.

Moreover, the relevant contaminant concentrations for fuel cell vehicles are still unknown. The concentration of a number of contaminants are determined by stationary measurement networks. However, the number of these stations is small. Especially data from highly trafficked streets, tunnels and motorways, where fuel cell vehicles actually move, are lacking. Here, in the exhaust of combustion engines, the contaminant concentrations can reach high peak concentrations [1]. Consequently, the concentrations have to be determined directly in urban traffic while driving. Besides, the air flow rate of the fuel cell vehicle defines the amount of contaminant that attains in the vehicle's fuel cell system. It is mainly dependent on the velocity of the vehicle and thus on the type of street and has to be likewise evaluated.

The present study therefore aims at systematically analyzing the influence of NO, NO_2, NH_3 and SO_2 on automobile fuel cells under realistic conditions. Two different types of fuel cells with a high and a low platinum loading were used in automobile short stacks with ten cells each. Four stacks were always tested in parallel in a four-stack test bench to ensure best comparability of the results. The operating conditions were selected in such a way as to be in the range of the conditions used in fuel cell vehicles. Two different experimental setups were developed. At first, four stacks were tested for more than 1500 h in a semi-dynamic way with different air contaminants. In these tests, only one of the relevant operating parameters like the temperature or the pressure was dynamically varied while the other parameters were fixed at a medium level. In a second experimental approach a real driving cycle gained from an existing course near Stuttgart, Germany was used to create full-dynamic tests. In these experiments four stacks of the high platinum load fuel cell type were employed for 365 h and four stacks of the low load fuel cell type were employed for another 716 h. Additionally, contaminant concentration measurements directly on the test course are evaluated and compared to the results from the test bench. Due to the realistic experimental setup and the huge scope of more than 2500 h of testing 12 fuel cell stacks and four air contaminants, a reliable prediction of the influence of urban air on fuel cell vehicles can be made.

1.1. State of knowledge – air contaminants

SO_2 is maybe the most intensively studied air contaminant due to its strong and irreversible impact on PEMFC [2–5]. Power losses from 15% up to 80% could be observed [6–9]. It is mostly assumed that SO_2 adsorbs directly on the platinum of the catalyst and thus reduces free sites

for the oxygen reduction reaction (ORR) [8,10]. The subsequent operation of the fuel cell with clean air is not suitable as a regeneration in most cases. To recover the damage of the fuel cell, extended actions have to be taken. An improved regeneration could be achieved by an expanded potential range, for example, due to cyclic voltametry measurements [4,11,12]. The SO_2 concentration in the EU will presumably further decline due to technical measures and the use of low-sulphur fuels. On the other hand SO_2 emissions in Asia and Africa have not reached a peak yet and a further increase is possible [13].

Many studies also examine the influence of NO_x on the cathode of PEMFCs. Most times a strong but reversible power loss of up to 60% is observed because of 1–25 ppm NO_x [14–20]. St. Pierre et al. supposed that the power loss is due to the adsorption of NO_x as NO at the Platinum of the catalyst in different configurations [21]. The effect of NO and NO_2 seems to be only slightly different [22]. Furthermore, an irreversible damage due to low concentrations and long operating times has sometimes been shown [10]. St. Pierre et al. and Mohtadi et al. expected that NO_2 can be reduced to NH_4^+ [18,21]. NH_4^+ negatively affects the membrane by occupying the perfluorosulfonic acid groups [23,24]. Therefore, a degradation of the membrane due to NO_2 as NH_4^+ can be assumed. It could be shown that 70–80% of the NO_x emissions of the passenger car sector is emitted by diesel engines [1]. The latest EURO-6-emission standard significantly reduces the limit for NO_x for all new passenger vehicles. Furthermore, due to the current public debate about NO_x emissions of diesel engines and driving bans, the number of diesel passenger cars is likely to decrease. Therefore, the concentration of NO_x in the EU will also presumably further decline in the future.

The negative influence of NH_3 on the cathode of PEMFC has also been examined by several groups [15,17,25–29]. The influence of NH_3 seems to be weaker but only partly reversible by clean air. Halseid et al. suggested, that NH_3 is partly adsorbed at the platinum and is oxidized to a nitrogen oxide [30]. This reaction leads to the spontaneous reversible performance degradation. Furthermore, in alinement with NO_2, it is supposed that NH_3 reacts as NH_4^+ with the perfluorosulfonic acid groups of the ionomer especially in the membrane [31–33]. The resulting performance loss is irreversible and leads to consecutive damage of the fuel cell.

In contrast to the other pollutants, the concentration of NH_3 in the air is most likely to increase in the next years. For the actual car fleet in Germany it could be shown that NH_3 emissions amount to about 10% of the NO_2 emissions [1]. These emissions are mainly caused by an unopposed side reaction in the three-way catalytic converters. To meet the EURO-6-emission standards for NO_x, a selective reduction catalyst (SCR cat) is needed in the new diesel passenger cars. The SCR cat converts NO_x to CO_2 or N_2 with the help of urea or ammonia as a reductant. To enable a sufficient reaction rate, ammonia has to be dosed with a stoichiometric ratio > 1. Therefore significant NH_3 slip can be expected. NH_3 emissions up to 1 ppm could be shown for a new diesel passenger car by Wegener et al. [34]. For this reason the NH_3 emissions from traffic will increase in the next years and NH_3 will get probably increasingly important as an urban air pollutant.

2. Experimental

2.1. Four-stack test bench

The experiments were conducted on a special test bench at the Center for Solar Energy and Hydrogen Research Baden-Württemberg (ZSW). The test bench was built by MS2 Engineering und Anlagenbau GmbH for four automobile short stacks with ten cells in parallel. All four stacks join the same pressure control by using one central pressure controller. Three of the four stacks also have a common cooling system. Humidification is done using bubble humidifiers with automated water replenishment for three stacks. Only one stack is humidified by an evaporator. The contaminant gases are separately supplied for each

Table 1
Characteristics and differences of the used fuel cells.

parameter	fuel cell type 1	fuel cell type 2
active area	300 cm^2	300 cm^2
platinum loading cathode	0.4 mg cm^{-2} Pt/C	0.25 mg cm^{-2} Pt/C
platinum loading anode	0.1 mg cm^{-2} Pt/C + RuO$_2$	0.1 mg cm^{-2} Pt/C
membrane	polytetrafluoroethylene-based material with perfluorinated sulphonic acid, thickness: 18 µm	polytetrafluoroethylene-based material with perfluorinated sulphonic acid, thickness: 15 µm
bipolar plates	graphite, straight channels	metal, serpentine-shaped channels

stack downstream the humidifier to ensure that the gases are not washed out. The joint pressure control and the joint cooling system lead to little constraints in the dynamic of the operation of the test bench. On the other hand, the test bench offers several advantages. Four test protocols can be conducted in parallel with different contaminant gases or contaminant concentrations. One stack can be used in a baseline measurement without contaminant supply as a direct reference. For these reasons the test bench is particularly suitable for comparative measurements of various pollutants and low concentrations and was therefore used for the present experiments.

2.2. Fuel cells and operating conditions

To explore the influence of the reduction of the platinum loading, two different types of MEAs (membrane electrode assemblies) and bipolar plates were used. The main difference is a lower platinum loading on the cathode of MEA type 2. Besides, the structure of the catalyst and the thickness of the membrane are different, as can be seen in Table 1. The type 1 MEA has a carbon carrier with a smaller but well defined surface with only few defects. It also has a higher content of ionomer in the catalysts, which has a lower conductivity due to a different structure. The configuration of the two types of fuel cells is shown in Table 1.

In order to create automobile conditions, the flow rates were controlled by the (resulting) current, i.e. only the amounts of oxygen and hydrogen needed for a specific load point was fed in. The operating conditions can be seen in Table 2.

2.3. Experimental setup – semi-dynamic tests

To receive further information about the influence of a dynamic operation on the influence of air contaminants a semi-dynamic test was developed. In former studies the influence of different operating conditions has been examined [20] and four relevant parameters have been identified. These parameters are the current density, the system pressure, the temperature and the relative humidity. In the semi-dynamic tests, one of these parameters was varied as fast as possible for 5 h in the following realistic ranges:

- Current density: 0.01–1.5 Acm^{-2}
- System pressure: 1.1–2.5 bar$_a$
- Temperature: 50–90 °C
- Relative humidity: 50–100%

The other parameters were fixed at standard conditions for 0.7 Acm^{-2}. To facilitate the evaluation, a short period with constant operating conditions was added at the highest, the lowest and at the mid point of each parameter variation. Furthermore, at the start of each test, the fuel cell stacks were conditioned with static operation with contaminants for 2 h and current-voltage characteristics have been recorded. At the end of each test a special cleaning procedure was employed. It included a variation of the current and simultaneously a high temperature or humidity to ensure a good regeneration of the fuel cells. Fig. 1 shows the sequence of individual semi-dynamic tests with its different sections in detail.

Four stacks were used for the semi-dynamic tests. The first 450 operating hours with the initially increased basic degradation were cut-off and not evaluated. One stack was used in a baseline measurement and was operated without contaminant as a reference for all 1560 h. The second stack was operated with NH$_3$ and different concentrations. The third stack was initially operated with NO$_2$ but was changed to SO$_2$ in the course of the tests. Prior to the change to SO$_2$, the third stack was interchanged with the fourth stack which until then had been operated with NO. This interchange was done to exclude an influence of the specific testing slot of the test bench. Due to these changes, one stack was operated with NO$_2$ at first and later with NO, while another stack was operated with NO first and later with SO$_2$. The course of all tests is shown in Fig. 2.

2.4. Experimental setup – authentic driving cycle

For the dynamic tests, a real driving cycle was used. This cycle is an existing course of 93 km near Stuttgart, Germany and is used by the Journal „auto motor und sport" to determinate the fuel consumption of test vehicles [35]. This course was used because it combines all different types of streets like urban traffic or highways. It also has a

Table 2
Operating conditions as a function of the current.

parameter	unit	operating conditions									
current	A	OCV	3	18	30	60	150	210	300	360	450
current density	Acm^{-2}	0.00	0.01	0.06	0.10	0.20	0.50	0.70	1.00	1.20	1.50
hydrogen											
stoichiometry	–		15.00	3.40	2.60	1.90	1.65	1.65	1.65	1.65	1.65
pressure	bar$_a$	1.2	1.24	1.27	1.30	1.45	1.77	2.05	2.45	2.70	2.90
relative humidity	%	66	66	79	84	94	95	93	95	91	92
air											
stoichiometry	–		16.00	3.60	2.70	1.90	1.65	1.65	1.65	1.65	1.65
pressure	bar$_a$	1.08	1.08	1.10	1.12	1.17	1.47	1.74	2.10	2.35	2.50
relative humidity	%	63	63	66	68	74	83	83	78	75	70
cooling											
stack temperature	°C	68	68	68	68	68	68	68	68	68	68
temperature difference inlet - outlet	°C	0.0	0.3	1.5	2.5	7.0	11.0	12.0	13.0	13.0	13.0
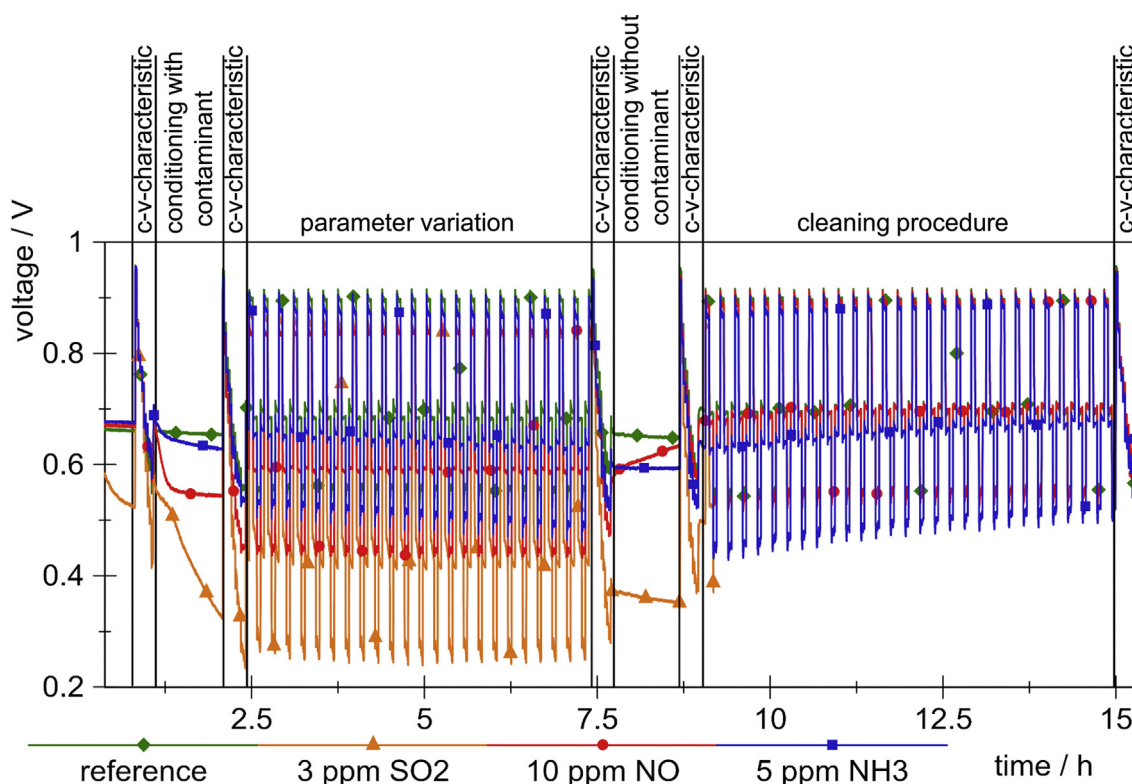
Fig. 1. Sequence of the semi-dynamic tests with explanation of the individual sections; current density variation is shown by the voltage as a function of the time. Blue curve, square markers = resulting voltage due to the injection of 5 ppm NH_3, red curve, round markers = resulting voltage due the injection of 10 ppm NO, orange curve, triangular markers = resulting voltage due to the injection of 3 ppm SO_2, green curve, diamond markers = resulting voltage of a reference measurement without contaminant. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
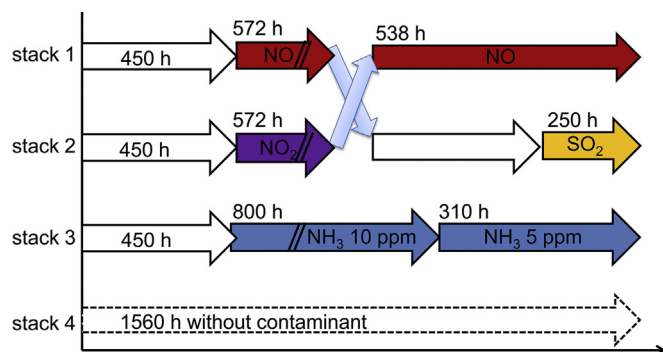
Fig. 2. Overall course of the semi-dynamic tests with stack interchanges, used contaminant gases and testing time.

challenging acceleration and inclination profile. The known acceleration and inclination profile was translated into a profile for the test bench. In addition, this profile was stretched until one run lasted 360 min. This was done to always ensure a good supply of the fuel cell with media and solely detect the negative influence of the contaminant gases. Since the profile was still very dynamic, current-voltage characteristics were recorded before and after each test. Additionally, short static operation phases were added to allow a meaningful evaluation of the data. Sometimes the test bench was shut down between the individual tests and sometimes several tests were executed consecutively. This was done to eliminate the influence of the overall test sequence. The course of the test profile can be seen in Fig. 3.

The tests were carried out with two different types of fuel cells to reveal the influence of a reduced platinum loading. The first experiments were conducted for 365 h with high loading MEAs (0.4 mg cm^{-2} Pt/C on the cathode side) and the contaminant gases NO, NO_2 and

NH_3. After the first 165 h of testing, experiments were carried out with only 91% H_2 and additionally 9% N_2 on the anode side. This was supposed to simulate the depletion of hydrogen due to the recirculation in fuel cell vehicles. The use of diluted hydrogen does not show any influence on the basic degradation or the effect of the contaminants. For this reason, all subsequent experiments were conducted with 91% H_2.

After 365 h the MEAs were changed to low loading MEAs (0.25 mg cm^{-2} Pt/C on the cathode side) and operated for 393 h with different concentrations of the contaminants NO, NO_2 and NH_3.

3. Results and discussion of the semi-dynamic tests

3.1. General findings

Fig. 1 shows the course of a semi-dynamic tests with 5 ppm NH_3 (blue curve, square markers), SO_2 (orange curve, triangular markers), a reference measurement without contaminant (green curve, diamond markers) and 10 ppm NO (red curve, round markers) as an example. It can be seen that most of the voltage drop already occurs at the constant conditioning phase early in the experiment for both contaminants. In the case of NH_3, the voltage drop takes a rather flat course and continues to decline through all the parameter variation. NO causes a steep, exponential voltage drop, as it is fast and reversibly adsorbed on the platinum catalyst. After a certain period of time, there is an equilibrium between adsorption and desorption. This equilibrium is not significantly influenced by the variation of the operating parameters, therefore the voltage drop does not continue in the course of the tests. In case of the nitrogen oxide, the voltage recovers quickly close to the level of the reference, as soon as the supply of the contaminant is stopped. A cleaning procedure therefore is unnecessary. SO_2 (orange curve with triangular markers) exhibits a similar steep voltage drop at the start of the experiment but due to the strong irreversible adsorption
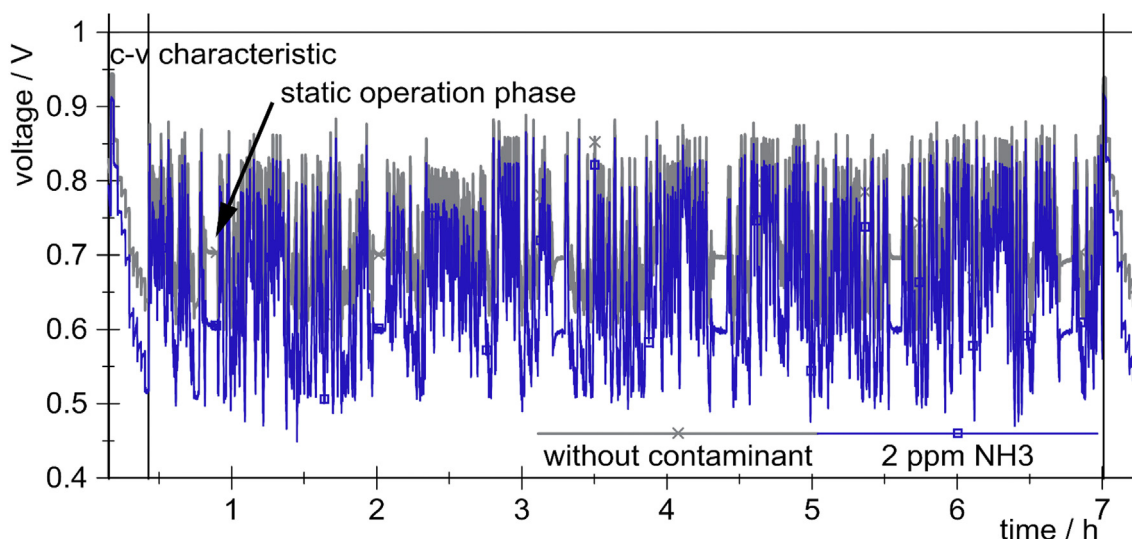
Fig. 3. Course of the driving profile – voltage as a function of time; Blue curve with square marks = 2 ppm NH$_3$, grey curve with cross mark = without contaminant. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

at the platinum catalyst no recovery can be achieved, neither at the constant recovery phase, nor during the cleaning procedure. Since this is one of the later tests, the irreversible voltage decrease can be seen by the lower start voltage compared to the other curves. In the case of NH$_3$, the voltage recovers only during the cleaning procedure.

For the reversible degradation it could be shown that both 10 ppm of NO and NO$_2$ cause voltage losses at constant current density of 20% on average in about 7 h of contaminant supply. 5 ppm NH$_3$ cause a voltage loss of 13% and 10 ppm NH$_3$ cause a voltage loss of 18% until the end of the contaminant dosing phase. As explained before, most of this degradation is reversible by the operation with clean air. In this regard SO$_2$ shows a different behavior because it is at least partially irreversibly adsorbed at the catalyst. Solely shutting down the test bench causes a remarkable recovery of the voltage. A shut-down of the test bench has a positive effect in so far as higher cell potentials are reached and an oxidation of the adsorbed SO$_2$ is caused [12].

These findings reveal the typical differences in behavior of the different contaminants as shown in former studies (e.g. Refs. [20,22]).

3.2. Influence of the operating conditions

Due to the parameter variation, the semi-dynamic tests provide findings about the influence of the operating conditions during the supply of the contaminants. For the evaluation of the degradation rates the voltage values of all tests were averaged. As a result of this evaluation, the degradation rates at the fix points of the parameter variations can be compared. At these fix points, a short period with constant operating conditions was added at the highest, the lowest and at the mid point of each parameter variation to achieve stable conditions for the evaluation. Fig. 4 shows the degradation in mVh^{-1} at the different operating conditions for all tests with 5 ppm NH$_3$ (310 h), 10 ppm NO (1110 h) and without contaminant (1560 h) including error bars.

As Fig. 4 shows, the supply of 10 ppm NO during the parameter variation does not have a negative influence exceeding the basic degradation of the fuel cell. The reason is the previous voltage drop in the first conditioning with contaminant at the start of the test (20% or 88 mVh^{-1}, compare Fig. 1). In this sequence of the test the fuel cell has already reached the equilibrium where adsorption and desorption outweigh each other. Besides this finding, some of the test parameters like the humidity of the fuel cell clearly have an influence on the degradation due to NOx as it was shown in former studies for example [22]. The tests with 5 ppm NH$_3$ show a different behavior with a

continuing voltage drop in the parameter variation sequence and will therefore be exemplarily evaluated in detail in the following section.

The degradation rates during the temperature variation reveal a slight dependence with a negative influence of a higher temperature, as can be seen in Fig. 4. Due to the specific setup of the test bench, a higher temperature leads to a slightly reduced relative humidity. A higher temperature simultaneously causes a decrease of liquid water in the fuel cell. Therefore, less NH$_3$ is dissolved and washed out of the cell. The individual course of the voltage during single tests reveal a dependence of the voltage on the relative humidity. Accordingly, it is assumed that the lower amount of liquid water is responsible for the negative effect of the higher temperature during the supply of NH$_3$.

The variation of the relative humidity and the system pressure shows a clear dependence with a positive influence of a high relative humidity and a high pressure. The positive effect of a high relative humidity is clearly based on the good solubility of NH$_3$ in water [37]. However, in the case of the variation of the pressure, an increased overall pressure increases the partial pressure of the NH$_3$. This increases the dissolution of NH$_3$ in the water phase. Furthermore, an increased overall pressure also increases the dew point which leads to more liquid water and therefore a further dissolution of NH$_3$. NH$_3$ has the best solubility in water of all used contaminant gases. In addition, it reacts with water to NH$_4^+$ and the acidic environment of the fuel cell shifts the reaction balance, so even more NH$_3$ can be dissolved. In summary it was found that the amount of liquid water is the decisive factor as for the strength of the effect of NH$_3$ for all parameters.

It was stated that the negative effect of NH$_3$ is due to a combination of effects [22]. In the short term NH$_3$ is partly adsorbed as a nitric oxide and in the long term it is additionally reacting with the per-fluorosulfonic acid groups of the ionomer which causes an increasingly irreversible damage of the fuel cell [22]. As a result, the voltage drops more slowly than in case of the other pollutants and the regeneration in the tests is often incomplete without a specific cleaning procedure.

In summary, it can be found that these results regarding the influence of the operating conditions in the semi-dynamic tests generally confirm former findings. The results still contain useful information for the development of an improved operating strategy to extenuate the influence of air contaminants on vehicles. However, due to the long testing times of the semi-dynamic tests the evaluation of the long term influence is of particular interest and will be presented in the next section.
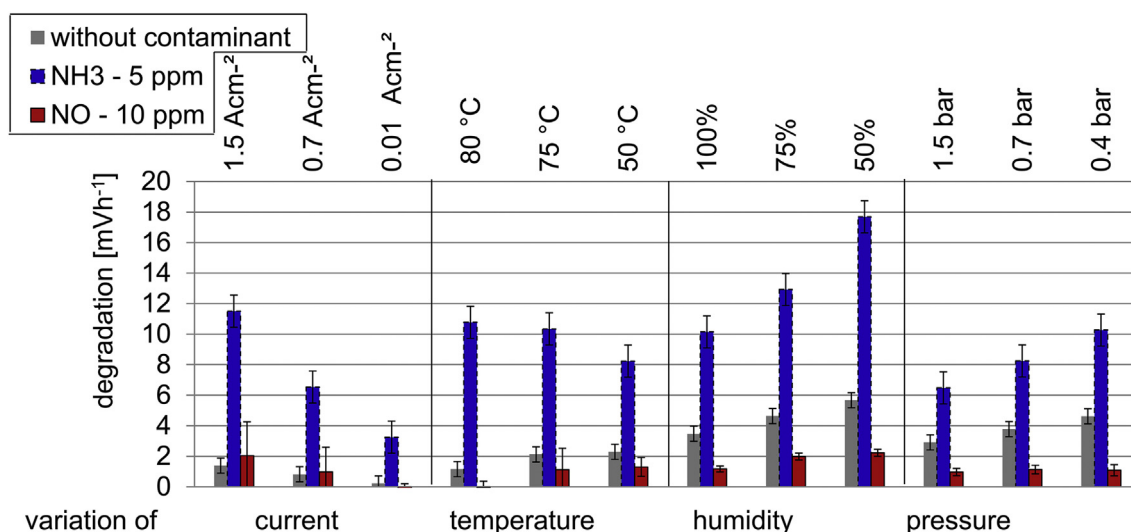
Fig. 4. Averaged degradation of voltage in mVh^{-1} due to the addition of 5 ppm NH_3 and 10 ppm NO at the parameter variation including error bars. Basic degradation without contaminant is added as a reference.

3.3. Irreversible degradation in the semi-dynamic tests

The long operating time of the stacks during the present tests particularly provides an insight into the irreversible damage or the long-term effect of the contaminant gases on PEMFC. For this evaluation of the irreversible damage, the voltages of the first and last tests are averaged for each stack. For this purpose, the voltage after the conditioning phase was selected at the start of the test or directly before the supply of contaminant gas, because this point is least affected by the previously used pollutant. Table 3 shows the irreversible degradation in 1560 operating hours of the semi-dynamic tests.

Table 3 shows that SO_2, NH_3 and NO/NO_2 cause an irreversible degradation of the cell voltage, which deviates significantly from the basic degradation of the stack without pollutant. The highest irreversible degradation of 19% is caused by SO_2 (which is equivalent to a degradation rate of 1.2 V per mol SO_2). This confirms the irreversible effect, especially because the quantity of SO_2 is significantly lower than that of all other pollutants (0.06 mol SO_2, see Table 3). The other two stacks showing a significant irreversible degradation have been subjected to significantly higher levels of pollutant (0.63 mol of NO_x and 0.56 mol NH_3). Nevertheless, the irreversible degradation of these stacks is high, too. Especially if the requirement for a maximum reduction of performance of 10% in 5000 operating hours for automobile applications is taken into account [38].

The high degradation rate of the stack operated with NO and NO_2 for more than 1000 h is of particular interest. It was stated before that NO_x most likely causes irreversible damage after numerous operating hours (e.g. Ref. [10]). The degradation is presumably caused by an inhomogeneous damage of the fuel cell by the NO_x and a shift of the oxygen reduction reaction towards the outlet of the fuel cell [22]. Due to the higher temperature the degradation mechanisms are more

pronounced at the fuel cell outlet anyway, and are further accelerated by the intensive use. It is assumed that this shift occurs at all catalyst-oriented contaminants and thus can be expected for hydrocarbons, too [22]. The present experiments prove an irreversible damage due to long term exposure to NO_x. Since the effect of NO and NO_2 is very similar, it can be assumed that an irreversible damage can be caused by both substances. This is a very important finding because of the high NO_x concentrations in urban areas.

In summary it can be asserted that all tested contaminants can cause an irreversible damage of the fuel cell. The highest irreversible damage is caused by SO_2. However, NH_3 and NO_x lead to significant degradation rates too, at least after several hundred operating hours.

Although the semi-dynamic experiments provide interesting findings especially because of the huge amount of individual tests, they are not suitable to assess the relevance of air pollutants for real fuel cell vehicles in urban areas. The necessity of realistic experiments could be shown before [19]. It was revealed that a realistic test setup and a control based on real vehicle operation is indispensable. Likewise, there is a need for vehicle-related fuel cells and real load cycles that have to be tested for several 100 h. For this reason, vehicle-related testing with a real driving profile has been carried out and is shown in the following section.

4. Results and discussion of the authentic driving cycle

4.1. General findings

The course of two individual tests with 2 ppm NH_3 and without contaminant as a reference can be seen in Fig. 3. The two c-v characteristics and the short static operation phases are marked. A comparison of the two curves reveals that 2 ppm NH_3 lead to a significant

Table 3
Irreversible degradation in the semi-dynamic tests with used contaminants and testing time. The degradation value is the difference between start- and end-voltage of the tests in percent.

stack/time	contaminant [g]/[mol]		start voltage [V]	end voltage [V]	degradation [%]	Degradation [mVg^{-1}]
reference/1.560 h	–		0.651	0.648	0.5	–
NO (new)/572 h	9	0.3	0.678	0.672	1	0.7
NO (after NO_2)/1.110 h	11.5	0.38	0.679	0.613	10	5.7
NO_2/572 h	11.3	0.25	0.668	0.656	2	1.1
SO_2/572 h	3.7	0.06	0.670	0.544	19	34.2
NH_3/1.110 h	9.6	0.56	0.680	0.632	7	5

voltage drop. The c-v characteristics are used to assess the long term degradation and the short static operation phases are used to evaluate the reversible short term voltage loss.

Most findings of the semi-dynamic tests can be confirmed by the full dynamic tests with the same MEAs. The stack that is operated with clean air shows a slightly higher basic degradation. In both test types 10 ppm of the nitrogen oxides are leading to approximately 20% voltage loss before the stacks are reaching the equilibrium.

NH_3 also causes very similar spontaneous damage to the fuel cell. However, in contrast to the semi-dynamic tests there is no specific cleaning procedure or extended regeneration phase. Only the final c-v characteristic and an eventual shut-down of the test bench serves as a partial regeneration. This is also reflected in the increased irreversible degradation, as shown in the following section.

4.2. Irreversible degradation

For the evaluation of the irreversible degradation, voltages of the first and subsequent tests are averaged for each stack. For this purpose, the voltage after conditioning at the start of the test or directly before the supply of contaminant gas was selected because this point is least affected by the previously used pollutant.

Table 4 shows the irreversible degradation of the stacks with the high platinum load in 365 h.

The 2.5% basic degradation without the use of contaminant is relatively high, especially compared to the value of 0.5% from the semi-dynamic tests. This is caused by the increased basic degradation in the first 200–500 operating hours of new MEAs. This increased degradation is induced by an increased agglomeration of the platinum and other effects until a stable structure of the catalyst is reached. In the semi-dynamic tests the first 450 h are not accounted for the evaluation, the irreversible degradation is therefore lower.

The nitrogen oxides do not cause an irreversible degradation exceeding the basic degradation in 365 operating hours. This confirms the results of the semi-dynamic tests where an irreversible degradation due to the nitrogen oxides was only observed after more than 1000 operating hours. NH_3 shows a voltage decrease of over 4% and thus a slight irreversible degradation. This result is lower than the 7% degradation of the semi-dynamic tests. However, the semi-dynamic tests include significantly higher testing times and pollutant masses used. If the degradation is compared in relation to the mass of contaminant, a voltage drop of $20 \, \text{mVg}^{-1}$ NH_3 can be seen in these tests. If this value is corrected for the basic degradation, $8 \, \text{mVg}^{-1}$ NH_3 are left. This value still exceeds the value of the semi-dynamic tests of $5 \, \text{mVg}^{-1}$ NH_3 and therefore exhibits a higher irreversible degradation in the tests with the realistic cycle.

In addition, new stacks with low platinum load MEAs ($0.25 \, \text{mg cm}^{-2}$ Pt/C) were employed for 393 h with the realistic driving profile. Before these experiments the stacks were used for further tests with contaminants for 323 h. The stacks with NO and NH_3 where not used with different contaminants as well as the reference stack was operated without contaminant. Only the stack with NO_2 was formerly supplied with toluene. It was assumed that toluene as a catalyst-affine

contaminant shows a similar behavior as NO_2 and therefore does not falsify the results. In summary 1.57 g NH_3, 4.85 g NO and 0.65 g toluene have been supplied in the former tests.

Table 5 shows the irreversible degradation of the stacks with lower platinum loading in 393 h with the realistic driving profile. As a comparison, the averaged voltage at the beginning of the fuel cell life has been added as well as the degradation since then (in grey).

With regard to the voltage levels of the new MEAs, all stacks lost a lot of their initial performance. It was especially the stack operated with NH_3 that experienced a very high irreversible degradation already. The stacks supplied with the nitrogen oxides didn't show a degradation exceeding the basic degradation.

This particular MEA type is known for its high initial basic degradation caused by its large and therefore sensitive surface area. Because of this high initial basic degradation, the tests of the first 323 h are not evaluated in this study.

If the irreversible degradation is calculated with the start-voltage after 323 h, the present tests generally confirm the findings of the former experiments with the high load MEAs. After the initial increased degradation the performance loss without contaminant is very low. The performance loss caused by the nitrogen oxides doesn't exceed the basic degradation either. Only NH_3 causes a strong irreversible degradation. With regard to the dosed amount of contaminant it accounts for $50 \, \text{mVg}^{-1}$ NH_3 and therefore is the highest degradation of all tests ($20 \, \text{mVg}^{-1}$ NH_3, $8 \, \text{mVg}^{-1}$ NH_3 corrected for the basic degradation with the high load MEAs and $5 \, \text{mVg}^{-1}$ NH_3 in the semi-dynamic tests). This high irreversible degradation is due to the differences of the MEAs and will be explained in the next section 4.3.

4.3. Comparison of the different MEAs

For the first 365 h MEAs with a loading of $0.4 \, \text{mg cm}^{-2}$ Pt/C on the cathode side were used with the gases NO, NO_2 and NH_3. Afterwards the stacks were changed to low loading MEAs with $0.25 \, \text{mg cm}^{-2}$ Pt/C for 393 h with NO, NO_2 and NH_3. Both stacks operated without contaminants show a similar behavior, solely the performance of the low load MEA is higher at the start of the tests. This can be seen in Fig. 5 when the two c-v characteristics of the new stacks at the start of the tests are compared. On the other hand, a significant difference in the effect of the contaminants can be seen. In the experiments with the low load MEAs all contaminants only lead to about half the reversible damage of the former tests with the high load MEAs. For example 10 ppm NO is only leading to 10% voltage loss on average before an equilibrium without further damage is reached. In contrast, the regeneration for the catalyst affine contaminants is significantly reduced and almost exclusively takes place during the shut-down phases.

The reversible damage due to NH_3 is also reduced to about 40% but the recovery of the voltage after the supply of the contaminant is not reduced. This is a contradiction to the increased irreversible performance loss of the stack, which is exclusively caused by NH_3. The more pronounced irreversible degradation is shown in Fig. 5, when the two c-v characteristics after about 360 operating hours are compared. In these 360 operating hours a similar amount of NH_3 was dosed in both cases. Nevertheless, the characteristics of the low load stack show a heavily increased difference and therefore a much stronger irreversible degradation of the stack.

Thus the reduced platinum loading leads to a reduced reversible performance decrease for all contaminants and an inhibited regeneration for the catalyst affine contaminants. This conclusion is contrary to the assumption that a reduced platinum loading leads to increased harmful effects. In the case of 10 ppb SO_2, for example, a reduction of 0.4 to $0.3 \, \text{mgcm}^{-2}$ Platinum has been shown to cause a more severe damage to the fuel cell [39]. But the MEAs used in the present work not only differ in the platinum loading but also in the carbon support, as shown in Table 1. The MEAs with the high platinum loading have a carbon carrier with a smaller but very well defined surface and only few

Table 4
Irreversible degradation of the high load stacks in 365 dynamic operating hours with the realistic driving cycle. The degradation value is the difference between start- and end-voltage of the tests.

stack	amount of contaminant [g]/ [mol]		voltage at the start [V]	voltage at the end [V]	degradation [%]	degradation [mVg^{-1}]
–	–		0.701	0.683	2.5	–
NO	3	0.1	0.700	0.691	1.3	0
NO_2	3.2	0.07	0.699	0.688	1.6	0
NH_3	1.4	0.08	0.695	0.666	4.2	20

Table 5
Irreversible degradation of the low load stacks in 393 dynamic operating hours with the realistic driving profile. The degradation value is the difference between start- and end-voltage of the tests. Contaminants, voltages and dosed amounts of the contaminant gases are shown.

stack	amount of contaminant [g]/ [mol]		voltage at start of life [V]	voltage at start of test [V]	voltage at the end [V]	degradation since start of test [%]	degradation since start of life [%]
–	–		0.745	0.690	0.690	0	7
NO	1.08	0.04	0.74	0.677	0.685	0	7
NO_2	1.53	0.03	0.739	0.692	0.682	1	8
NH_3	0.6	0.04	0.736	0.623	0.593	5	16

defects. There is also a higher amount of ionomer in the catalyst, which has a lower conductivity due to a different structure. The low load MEAs have a carbon carrier with a significantly larger surface and less ionomer with a higher conductivity in the catalyst. Also, the membrane differs as it is thinner in the low load MEAs. The tests without contaminant reveal that the low load MEAs generally achieve a better performance. On the other hand, the stability of the catalytic converter is apparently lowered, which causes the increased basic degradation without contaminant gases.

It is known that the structure of the carbon carrier has a major influence on the properties of the catalyst [40,41]. It mainly affects the electron transport from the platinum to the carbon [40]. It has been shown that the activity of the catalytic converter is more dependent on the accessibility of certain regions of its surface than, for example, on the particle size of the platinum [42].

In addition, it is known that the different reactions of the nitrogen oxides in a fuel cell are essentially influenced by the crystalline structure of the platinum [43,44]. It has even been shown that the adsorption of NO_2 as NO on platinum is able to change the structure of the platinum, at least in the short term [45]. Although these studies are not directly transferable to the situation in a fuel cell, they exhibit the importance of the structure of the carbon carrier. Therefore it can be assumed that this difference in the structure of the used MEAs is the reason for the reduced effect of the contaminants in the present tests.

On the one hand, the modified surface of the carbon carrier provides more accessible platinum places. This allows a relatively high ORR-rate even in the case of supply of contaminants. On the other hand, the modified crystal structure also causes other structures of the platinum and more defects at which the contaminant substances can be bound in other configurations. In combination these effects cause a reduced spontaneous voltage or current density loss, but also a reduced recovery of the low load MEAs. The same reasons are causing a reduced reversible power loss in the case of NH_3. What's more, it can be assumed that the reduced amount of ionomer - especially in the membrane - is leading to the increased irreversible degradation.

4.4. Contaminant concentrations in urban traffic

Another advantage concerning the utilization of a real course as the driving profile for these tests is the opportunity of comparing the results to the real contaminant concentrations in urban traffic. As part of a public project funded by the German Federal Ministry for Economic Affairs and Energy called "ALASKA" (Evaluation of Air Emission Scenarios for the design of air filters and cathode regeneration cycles for automobile fuel cells - 3ET6036A), the concentration of NO, NO_2 and NH_3 was measured at a high time resolution of 1 s with a mobile laboratory (MobiLab) while driving. These measurements provide insight to the average and peak concentration of the contaminants on the different street types and were used to evaluate the average burden of fuel cell vehicles to contaminants in Germany. For this purpose the different street types were summarized to the three sections "rural", "urban" and "highway", which are characterized by average speeds (i.e. air consumption of the fuel cell vehicle) and average pollutant concentrations. The air consumption of the fuel cell was also determined based on the test cycle, where the different street types can be easily distinguished. The measured concentrations of pollutants were then calculated proportionately. Furthermore, assumptions for the vehicles frequency and length of stay on the different types of roads were made. For the average passenger car, 33% in each section was assumed for example. Above that, various information on the use of vehicles is available [46]. These results and assumptions allow the calculation of the average contaminant burden for fuel cell vehicles in Germany, the detailed description can be found elsewhere [36]. The calculated burden can be directly compared to the results of the experiments using the low load MEAs in Table 6.

This comparison shows that the concentrations and loads of NH_3 used were higher than can be expected on average in urban traffic. However, peak concentrations of 1.8 ppm NO were measured on the standard driving cycle. Therefore, the applied concentrations and loads of NO and NO_2 are high but not unrealistic.

The findings from the present study can therefore be used in order to forecast the influence of the contaminants on fuel cell vehicles in
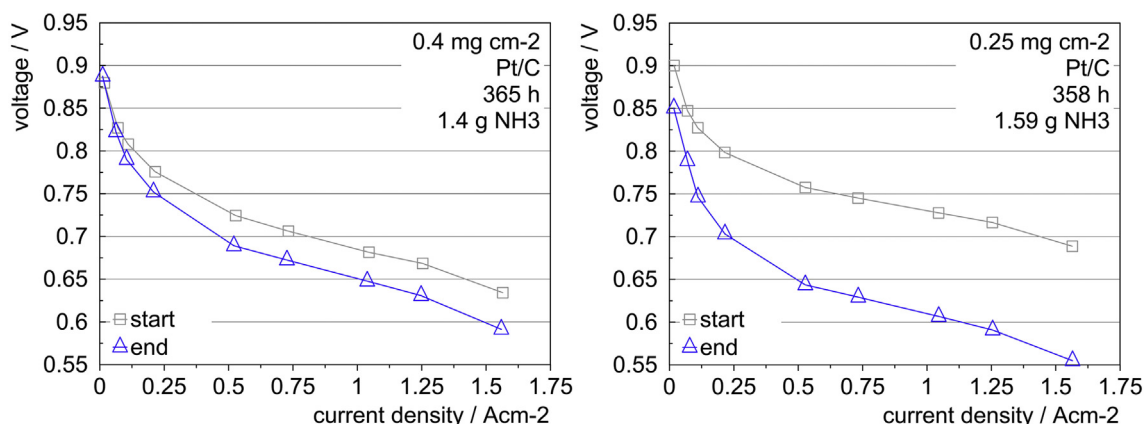
Fig. 5. Comparison of the two types of MEAs at start/after about 360 operating hours. C-v characteristics of stacks operated with NH_3 are shown, reflecting the irreversible degradation. Higher initial performance of the low-load MEA can be seen.

Table 6
Comparison of the concentrations and amounts of contaminants used in the realistic tests with low load MEAs and from the contaminant measurements on the standard driving cycle measured on November 8th, 2016. The amounts of contaminant are expressed in mg per active area of the electrodes of the fuel cell stacks to enable a direct comparison. The calculation of the average burden of fuel cell vehicles to contaminants in Germany is explained elsewhere [36].

contaminant	amount in test $[mgcm^{-2}]/[mmolcm^{-2}]$		concentration in tests [ppb]	average burden $[mgcm^{-2}]/[mmolcm^{-2}]$		average concentration [ppb]	Maximum concentration [ppb]
NO	0.36	0.01	2.000	0.37	0.01	219	1763
NO_2	0.51	0.01	2.000	0.26	0.01	81	628
NH_3	0.2	0.01	2.000	0.01	–	11	43
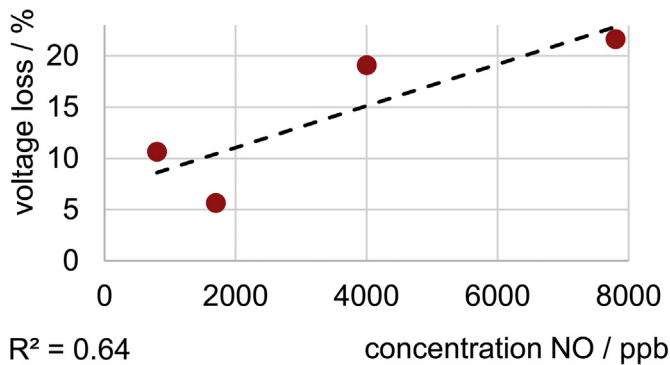
Fig. 6. Average voltage loss in percent from all experiments with NO and the realistic driving cycle as a function of contaminant concentration.
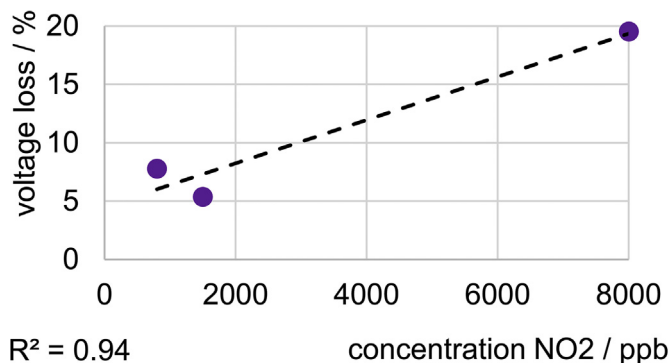

Fig. 7. Average voltage loss in percent from all experiments with NO_2 and the realistic driving cycle as a function of contaminant concentration.

Fig. 8. Average voltage loss in percent as a function of contaminant concentration from all experiments with NH_3 supplied to low load MEAs when using the authentic driving cycle.

urban areas. Figs. 6 and 7 show the averaged voltage drop in the tests on the realistic driving cycle in percent for NO and NO_2. The concentrations are specified with regard to the humid gas mass flow.

As the diagram shows, a voltage drop of about 20% is caused by 8 ppm NO and NO_2, respectively. 1 ppm of the nitrogen oxides still leads to 10% performance reduction. In combination with the air pollutant concentration data, the regression line can be used to estimate a voltage loss of 5% due to 219 ppb NO in urban areas. The same voltage loss of about 5% can be expected due to 81 ppb NO_2 on average. Only in exceptional situations, such as in traffic jams or in a tunnel, NO_x concentrations over 2 ppm occur. In these cases short-term performance losses of more than 10% have to be anticipated.

Fig. 8 displays all tests with NH_3 and the low load MEAs. In agreement with the nitrogen oxides a flat course of the regression line shows a proportionally strong influence of low concentrations. In combination with the air pollutant concentration data, a maximum voltage loss of 3% can be estimated due to 11 ppm NH_3 in urban air in the short term.

The influence of SO_2 cannot be determined precisely because tests with the realistic drive profile are missing. Nevertheless, it can be assumed that it will have a harmful effect, at least in the long term. Even though its concentration is low in urban air, it has been shown that SO_2
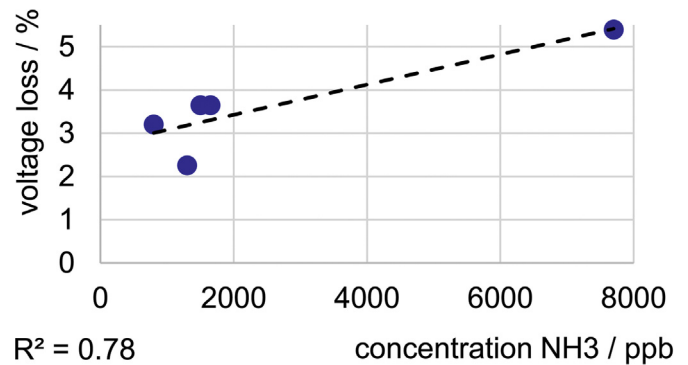
is accumulated at the catalytic converter. Some of the SO_2 is irreversibly bound to the catalyst and thus reduces the ORR rate of the fuel cell. Therefore it is rather a gradual irreversible performance loss than a strong, spontaneous reaction that is expected due to SO_2.

But even a slow irreversible degradation is relevant since it shortens the lifetime of the vehicle and thus endangers the cost target. In the present tests in addition to SO_2, particularly NH_3 caused an irreversible degradation of the fuel cell. It also can be seen that the sensitivity of the fuel cell towards NH_3 increases with increasing damage. The performance degradation therefore roughly follows an exponential function. In 716 operating hours, the stack has lost about 20% of its performance due to a total of 2.19 g NH_3. Due to the increasing irreversible degradation over the operating time and the influence of the contaminant concentration, the exact impact of ammonia remains uncertain. Nevertheless, it can be assumed that NH_3 will lead to a significant irreversible degradation of fuel cell vehicles in urban areas. In addition, the ammonia concentration is likely to increase in the next years due to the increasing number of diesel engines with SCR cats.

5. Conclusion

In the present study two types of experiments are presented. A semi-dynamic type of experiment was developed and used for 1560 h. Afterwards, an authentic driving cycle was used with two different MEA types for 365 and 716 operating hours. Due to the present tests, the influence of the operating conditions and the MEA type could be determined. For a reliable prediction of the influence of urban air on fuel cell vehicles there is not only the need for a realistic test setup and many operating hours but also for sound knowledge of the air quality on the streets. Therefore, the mixing of contaminants encountered on the authentic driving cycle was measured with a mobile laboratory. These results allow the calculation of an average contaminant burden for fuel cell vehicles in Germany. The calculated burden was compared to the results of the experiments with the authentic driving cycle.

In summary the present study therefore combines fuel cell tests under automotive conditions, long testing times and real contaminant concentration measurements on the streets for the first time. By this

combination it could be shown, that all tested pollutants - NO, NO$_2$, SO$_2$ and particularly NH$_3$ will have a significant negative influence on fuel cell vehicles in Germany. It may also be assumed that other pollutants, such as hydrocarbons, have a negative influence on fuel cell vehicles, too. For this reason further research and development regarding suitable filters and operating strategies against the negative influence of air contaminants are suggested.

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