



Article Investigation of Filtration Phenomena of Air Pollutants on Cathode Air Filters for PEM Fuel Cells

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Abstract: Filtration of cathode air is one of the challenges in operating proton-exchange membrane (PEM) fuel cells. The poisoning with air contaminants can lead to rapid performance degradation and initiate an aging process of the fuel cell. Various commercially available cathode filters are being tested in a laboratory gas test bench within the research project X-EMU (03B10502B and 03B10502B2). A literature review of harmful gas contaminants in the air used for the oxygen reduction reaction (ORR) on the cathode side was conducted. Experimental investigations took place at 40 °C with synthetic humid air containing low concentration contaminants such as ammonia, nitrogen dioxide, carbon monoxide, sulfur dioxide, hydrogen sulfide, and toluene. Test durations varied from 3 to 24 h depending on the filtration efficiency. Each gas contaminant showed different reactions with the investigated filters. The filters did not let sulfur-containing components pass. However, carbon monoxide could not be filtrated by any of the tested filters. The filtration of nitrogen oxides was not efficient for all tested filters, while additional filter materials were essential for a successful filtration of ammonia. Comparative results lead to a discussion of possible effects on a fuel cell with an outlook on optimization of the filtration behavior.

Keywords: PEM fuel cell; cathode air filter; air pollutant emissions; laboratory gas bench

1. Introduction

Due to their high efficiency, fast start-up, zero-emissions, high driving ranges, and short refueling times, fuel cell electric vehicles (FCEV) based on proton-exchange membrane (PEM) fuel cell systems represent a promising solution to reach the goal of sustainable mobility [1–3]. However, the breakthrough of fuel cells requires low total costs of ownership (TCO) and thus durable and reliable systems. To reduce the TCO of FCEVs, the service life of fuel cell systems needs to be increased significantly. Particularly for commercial vehicles with a required service life of 25,000 to 40,000 h, a replacement of the fuel cell system is out of the question for reasons of competitiveness [4]. Therefore, not only the design and the operating strategy of the fuel cell system must be improved, but also the protection of the fuel cell stack against environmental stressors must be ensured by preventive measures.

Preventing the intrusion of particulates and contaminants via the air and hydrogen processing systems in both the cathode and the anode of the fuel cell stack plays an important role [5,6]. Hydrogen (H₂) with a high purity of 99.999% (Hydrogen 5.0) provided by the hydrogen tank is used to minimize the probability of severe contamination of the fuel cell stack. On the air entry, filters are installed in front of the air-processing system as shown in Figure 1. Not only is particle filtration essential to prevent blockages within the gas diffusion layers (GDLs), but also chemical filtration of key air contaminants found in the ambient air such as NH_3 , SO_2 , NO_x , and CO and the use of as pure as possible hydrogen [7].



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Figure 1. Simplified generic layout of a fuel cell system including common measurement equipment.

Air management including the air filter is the second-largest cost factor of PEM fuel cell systems [8]. The investigation of required air filter efficiencies and hydrogen purities and the development of cost-efficient solutions require a closer look at the severity of relevant ambient contaminants as well as impurities introduced during the production of hydrogen. Most of the contaminants adsorb on the catalyst surface and lead to power losses due to the reduction of the electrochemically active surface area (ECSA) [9,10]. Furthermore, the water content within the membrane and ionomers and the protonic conductivity can be reduced if contaminants like NO_x or NH₃ or their breakdown products have a higher affinity to sulfonic acid groups than H⁺ [11,12].

However, while most contaminations can be reversed by dedicated regeneration procedures, some need to be considered in detail. This can be either caused by the fact that their presence leads to instantaneous and severe power losses in the short-term or even to irreversible degradation in the long term since a reversal within the operating range of the fuel cell system is not feasible. Current research is focused on both reversible voltage losses and irreversible degradation phenomena. On the anode side, the carbon monoxide (CO) content in the hydrogen is important since CO blocks the active area of the platinum catalyst. Catalyst poisoning by CO can, however, be reversed in contrast to contamination with sulfur species (H₂S, SO₂), which is more relevant on the cathode side. In addition, nitrogen oxides (NO_x), ammonia (NH₃), hydrocarbons (HC), volatile organic compounds (VOC), and particles (dust, salt) in the ambient air affect the performance of the fuel cell [10,13,14].

While the purity of hydrogen—defined by the ISO 14687 [15] and SAE J2719 [16] standards—needs to be monitored and ensured in the tank and at the filling stations by the station operators, the concentration of ambient contaminants is highly uncertain. The Institute of Energy and Climate Research Troposphere (IEK-8) of the Forschungszentrum Jülich measured the concentration of ambient air contaminants with a comprehensive gas

phase and particle analysis using a Mobile Lab (MOBILAB) [17]. With this equipment, the relevant pollutants in road traffic and the distribution of pollutants at a small scale were determined. Particularly in cities, highly variable pollutant distributions were measured with emission peaks adding up to the regional and local background as shown in Figure 2. In general, the emissions of automotive vehicles and industrial manufacturing processes represent the major sources of contaminants. Another source of contaminants is the auxiliary components like the metal bipolar plates [18]. The metal ions are either released during the manufacturing process or during operation by corrosion [6,19]. However, the focus of this work is put on the impurities in the ambient air.

Impurity source	Typical contaminant	-	
Air	N2, NOx (NO, NO2), SOx (SO2,	Emission peaks	
	SO3), NH3, O3		
Reformate hydrogen	CO, CO ₂ , H ₂ S, NH ₃ , CH ₄	Б	
Bipolar metal plates (end plates)	Fe ³⁺ , Ni ²⁺ , Cu ²⁺ , Cr ³⁺	rati	
Membranes (Nafion ®)	Na+, Ca ²⁺	Station value	
Sealing gasket	Si	(average)	
Coolants, DI water	Si, Al, S, K, Fe, Cu, Cl, V, Cr	C Local background	
Battlefield pollutants	SO ₂ , NO ₂ , CO, propane, benzene	Regional Background	
Compressors	Oils		

Figure 2. Major contaminants of the fuel cell system (left) [18] and contributions to the concentration of air pollutants in urban areas (right) [17].

Due to the highly uncertain pollution of the ambient air, the air filter of the fuel cell system needs to ensure a reliable filtration of any severe contaminants and reduce the influence of the ambient air pollutants on the fuel cell stack. Different contaminants are listed in Table 1. In the following, the effect of selected gaseous air pollutants namely carbon monoxide (CO), nitrogen oxides (NO_x), sulfur dioxide (SO₂), ammonia (NH₃), and toluene (C_7H_8) on the performance and degradation of the fuel cell system is discussed in detail.

Contaminant	Molecular Formular	Reversible Damage	Irreversible Damage
Sulfur dioxide	SO ₂	-	Catalyst poison
Nitrogen oxides	NO _x	Catalyst poison	-
Carbon monoxide	CO	Catalyst poison	-
Ammonia	NH ₃	-	Reduced H+-conductivity in the membrane
Hydrocarbons	C _x H _y	-	-

Table 1. Cathode degradation impact of air contaminants [20,21].

1.1. Carbon Monoxide

Carbon monoxide contamination plays a bigger role on the anode side than on the cathode side of the fuel cell, since a small concentration can remain in hydrogen in the production process [22,23]. On the cathode side, the influence of CO is much lower as it can be oxidized to CO_2 which can then leave the cell with the reaction products [24].

1.2. Nitrogen Oxides

Nitrogen oxides such as NO and NO₂ influence the fuel cell in a very negative but mostly reversible way [25–27]. Misz et al. reported reversible voltage drops during short-term and irreversible voltage drops during long-term experiments [26]. The performance can be reduced by two different mechanisms. NO_x can either be adsorbed on the catalyst's surface and competes then with the ORR which leads to a higher activation overpotential on the cathode side [28]. Another source of performance loss is that NO_x can be reduced

1.3. Sulfur Dioxide

The influence of sulfur dioxide is not only very negative but also irreversible. SO₂ is directly adsorbed on the catalyst which has the effect that Pt particles are blocked and are not usable for the ORR anymore [29,30]. Most scientific works agree on the fact that two different sulfur species are adsorbed, while one species causes irreversible and the other one reversible degradation of the fuel cell [31]. Reversible degradation causes weak adsorption forming Pt-SO₂ while irreversible degradation leads to strong adsorption forming Pt-SO and Pt-O [31]. However, the irreversibility of the strong adsorption has to be analyzed further due to the possibility of removing the SO-molecules from the catalyst surface with the help of an oxygen reaction [12]. The degradation is increased by several parameters such as a low operating temperature and relative humidity [25]. Moreover, the catalyst's design plays a role in this context, since a lower Pt loading leads to a higher degradation [12].

Additionally, a two-stage degradation process is mentioned in the literature regarding SO₂-contamination in fuel cells. In this process, a multi-layer of sulfur is formed on the catalyst's surface after the formation of a monolayer which leads to a second voltage drop during the operation with air contaminated with SO₂ caused by a slower ORR [29].

1.4. Ammonia

It is not completely understood how ammonia impacts the fuel cell's degradation. Several scientific works report a reversible degradation caused by NH₃, while others see an irreversible degradation [12,25]. Similar to the previously mentioned contaminants, NH₃ can also increase the ORR overpotential by forming NO via oxidation on the catalyst surface [9,12]. Moreover, NH₃ can react to NH⁴⁺ either by reacting "with water [...] or protons from Nafion" [12] on their way from the anode to the cathode. As already mentioned before, the lower water uptake of NH⁴⁺ compared to protons reduces the membrane's water content and therefore its proton conductivity [12]. A low temperature and relative humidity enhance the degradation effect [25].

1.5. Toluene

Toluene as a representative hydrocarbon has a negative but reversible impact on fuel cell performance. It is mainly adsorbed on the catalyst surface, which causes blocked Pt particles and therefore impedes the ORR [32]. Additionally, toluene changes the properties of the gas diffusion layer (GDL) and the catalyst coated membrane (CCM) as they become more hydrophilic [12]. This is caused by the formation of H_2O_2 as a result of the occurrence of toluene which reduces then the hydrophobicity of the GDL [32,33]. This impedes the water removal from the cell and leads to increased mass transport resistances [12]. Once more, low operating temperatures enhance this effect while also a higher current density and stoichiometry lead to an increasing degradation [9,34]. Another effect that has been detected is the formation of CO_2 after several reactions of toluene and intermediate products [12].

The influence of the above-mentioned contaminants has been studied in previous works on the fuel cell itself. The filtration efficiency of different cathode air filters has not been considered by measuring the individual gas concentrations upstream and downstream of each filter to allow a comparative analysis of the filters. For efficient cathode air filter development, the factors involved in identifying cathode air filtration mechanisms must be discussed comprehensively. Based on this knowledge, extending either filter exchange intervals or more robust fuel cell systems or both will be possible. Furthermore, the effect of each gas must be studied individually and in gas mixtures, as well as under different and adjustable boundary conditions, in order to build a model for cathode air filter behavior. For this reason, a test bench for catalyst investigations is adapted to carry out a comparative study for different types of cathode air filters under defined boundary conditions with higher reproducibility. These tests were executed within the research project X-EMU (03B10502B and 03B10502B2). In this project, a high-performance fuel cell drive for hybrid EMU multiple units was developed and validated in a modular traction system in cooperation with Siemens AG.

2. Results

After preconditioning of the filter samples, the filters, which are described in the materials and methods section, are challenged with air contamination. The results of the investigations with the total contamination are depicted in Figure 3. The concentration traces downstream of the filter for the species NO_x, NH₃, toluene, CO, H₂S, and SO₂ are compared for these three filters. The breakthrough thresholds for 5% and 10% as well as the concentrations upstream of the filter are plotted in the diagrams. Test durations $t_{test} = 10,000$ s are selected for a sufficient comparison.



Figure 3. Results of the investigations on different filters with the entire gas matrix.

The diagrams lead to the conclusion that all investigated air filters can clean pollutants such as SO₂ and H₂S with a concentration $\psi_{gas} = 1$ ppm from the cathodic air stream. Nevertheless, a 10% breakthrough of both gas contaminations could be detected in early phases with the dual-layer filter, which is kept certainly on the same level for the next 24 h. On the state-of-the-art (SOA) filter, a 10% SO₂ breakthrough is measured as well. In general, the filtration of both components is not crucial for all investigated filters. On the other hand, all filters exhibit no cleaning effect for CO emissions, so that CO measurement reaches the

value upstream of the filter instantly after switching the gas matrix to the sample. Further investigations with a CO concentration $\psi_{CO} = 5$ ppm upstream the filter show the same behavior on all filters. Therefore, they are not included in Figure 3. For ammonia and toluene, the investigated filters show different behaviors. For instance, the triple-layer filter can offer an enhanced performance in terms of removing both ammonia and toluene emissions from the air. Under the investigated circumstances, 10% breakthrough of the ammonia filtration on the triple-layer filter is detected first at $t_{NH_3,10\%} = 5.5$ h. Furthermore, the performance of the triple-layer filter is followed by the dual-layer filter, while the SOA sample cannot filter ammonia during these investigations. Therefore, additional filter materials are essential for the successful filtration of ammonia. Toluene emissions can be cleaned slightly better with the SOA filter in comparison to the dual-layer filter. In order to build up a worst-case scenario such as cold start hydrocarbon emissions from a gasoline engine in front of the fuel cell component, the filters are challenged with a relatively high concentration of toluene. However, it can be concluded that the toluene filtration behavior of all filters is not on a critical level.

Although the filters are challenged with NO₂, the NO_x emissions including NO and NO₂ are shown in Figure 3, because a reduction of NO₂ to NO is observed during the tests and NO is another pollutant for the fuel cell stack. All filters show low filtering efficiency with respect to NO_x species, which will be analyzed in detail below.

NO and NO₂ concentrations from the investigations in Figure 3 are separately examined in Figure 4. The NO₂ reduction behavior of the investigated filters is different. The dual-layer filter has a higher NO₂ slip at the beginning of the filtering phase, whereas the SOA and the triple-layer filter have a higher reduction performance, thus higher NO slip after the filtration process. NO and NO₂ traces are evaluated further on the isolated acid filter of the triple-layer filter during the whole filtering duration.



Figure 4. NO (filled) and NO₂ (blank) breakthrough from different filters with the entire gas matrix.

In order to investigate the long-term NO_x filtration behavior, only the acid filter from the triple-layer filter is challenged by NO₂ and the standard air composition including N₂, O₂, CO₂, and H₂O. In Figure 5, the results are depicted from the long-term investigations on the acid filter of the triple-layer filter with $\psi_{NO_2} = 10$ ppm for $t_{duration} = 26$ h (a) as well as $\psi_{NO_2} = 50$ ppm for $t_{duration} = 13$ h (b). After dropping below a filter efficiency $\eta_{Filter} = 30$ %, the tests are finished.

Both measurements start with an intensive reduction of NO₂ to NO in addition to a slight filtration. At a low NO₂ concentration upstream of the acid filter from the results in Figure 5a, a high NO slip can still be observed after 26 h of testing, while at high NO₂ concentrations upstream of the filter in Figure 5b the NO₂/NO balance is shifted to NO₂



species after approx. 8 h. In general, a high NO_2 slip from the filter is expected due to an increased NO_2 amount at the inlet.

Figure 5. Influence of long-term investigations on the acid filter of the triple-layer filter at $T_{\text{Filter}} = 40 \text{ }^{\circ}\text{C}$ with (a) $\psi_{\text{O}_2} = 10 \text{ ppm}$ and (b) $\psi_{\text{NO}_2} = 50 \text{ ppm}$ in the air mixture upstream of the filter.

Another investigation is carried out on the NH₃ filter of the triple-layer filter to understand the filtration mechanisms and check its regeneration behavior. The results are shown in Figure 6. In this measurement, the NH₃ filter is challenged with only $\psi_{\text{NH}_3} = 60$ ppm in addition to the standard air contamination. After dropping below a filter efficiency $\eta_{Filter} = 80\%$, NH₃ dosing is stopped and the filter temperature is slowly increased by electrical heating of the inlet gas. In accordance with the thermal management of fuel cell applications, a regeneration temperature of $T_{Regeneration} = 80$ °C is selected to keep the regeneration effort low.



Figure 6. Influence of interruption of ammonia challenge as well as the temperature increase on the NH₃ filter of the triple-layer filter with only ψ_{NH_3} = 60 ppm in the air mixture downstream the filter.

During the heat-up phase, neither NH₃ nor other species slipped through the filter. Subsequently, the gas and the filter are cooled down to $T_{Measurement} = 40$ °C and the filter is challenged by NH₃ again. However, the filtration of NH₃ is continued with the same breakthrough as well as the same filtration efficiency. Therefore, regeneration of this filter is not possible under these boundary conditions, so that the filter must be replaced for further use of the fuel cell.

3. Discussion

In these experimental studies, three commercially available filters were tested: a triple-layer filter and two dual-layer filters. The LGB investigations conclude that each contamination behaves differently on each filter. In order to distinguish the filtration mechanisms, each gas component is discussed separately in the following. The principle of all filter types is the physisorption of the pollutants on substrates with a big surface area (BET (Brunauer–Emmett–Teller) surface >> 100 m²/g). This will be supported by additional mechanistic systems: acid/basic chemisorption and catalytic reactions. No chemical storage reactions can be observed at the investigated temperatures.

The NO_x components (NO and NO_2) were only slightly filtered. With its basic surface, the acid filter supports the filtration mechanisms. The filtering of both NO_x components has to be improved for a robust application. The observed formation of NO from NO_2 is a catalytic process, most likely caused by the challenged filter itself, because filterspecific differences were detected under the same boundary conditions as can be seen in Figure 4. For a detailed explanation of NO_2 to NO reduction, further analyses such as energy-dispersive X-ray (EDX) analysis and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) must be considered within future works, in order to recognize intermediates in a NO_2/NO balance. NO_x species can also be removed from the filter via different methods as in other applications. In automotive exhaust gas after-treatment systems, lean NO_x traps store NO_x emissions at comparably very high temperatures above 200°C, which are converted into N_2 under rich conditions, mainly with CO as a reducing agent. Another option is a thermal regeneration of passive NO_x adsorbers, where NO_x emissions are released and converted into a downstream catalyst. Here, a similar regeneration of the filtered NO_x components to harmless products is not applicable, due to the absence of suitable reducing agents and due to the low filter temperatures. An electrical heater and a bypass line could regenerate the filters and release the NO_x emissions back into the ambient air. A more reasonable for the environment, but less practicable way would be to drain the filters externally via temperature or pressure shocks. With this, the contamination in the intake air does not exit into the ambient air again and the system setup literally cleans the air.

In the case of toluene, the only possible filter mechanism is physisorption in which the hydrocarbons are physically bound to the filter surface. Catalytic reactions would require much higher temperatures. For further improvement, the surface area of the filter can be increased. Active charcoal can also act as a reversible storage volume, as in the case with charcoal filters in the vent pipes of gasoline fuel tanks.

High filtration efficiencies can be achieved for H_2S and SO_2 . As mentioned earlier, these gas species cause very high damage to the fuel cell and they must be filtered from cathode air. Maintaining a sufficient filtration efficiency is very important and essential for the lifetime of the fuel cell.

A successful filtration of ammonia is possible. However, it requires an additional filter, because ammonia as a basic component needs an acid-coated filter material (e.g., NH_3 -filter of the triple-layer filter).

According to the literature, CO in the cathodic stream does not cause any direct impairment in the performance of the fuel cell. CO oxidizes in the presence of oxygen in the air to CO₂, which has also no influence on the performance initially. In the long term, however, CO₂ can induce in a liquid water phase the formation of carbonic acid $(H_2O + CO_2 \rightarrow H_2CO_3)$, which can potentially damage the conventional membrane ma-

terial. Further investigations are necessary to define an efficient filtration method for CO without forming CO₂.

The investigations have shown that a multi-layer concept is required since the gases in the air have different properties. This can increase the number of gases to be filtered and delay the aging of the fuel cell. Filtration efficiency can be improved by increasing the filter surface area.

In addition, a larger filter surface area can be created by increasing the porosity of the surface without changing the volume. For both solutions, packaging in the vehicle (installation space for the filter) needs consideration. In addition, the potential development of the backpressure and the increased power requirements of the compressor must be taken into account. For multi-layer filter applications, one approach is to design the individual layers very thinly to keep the filter volume in the desired range.

Ongoing and future activities will extend the range of testing to the dynamic behavior of air filters under realistic conditions in road and rail transport and to the effects of air pollutants on fuel cell stack performance and durability. In this regard, the concentration peaks of several contaminations caused by, e.g., a vehicle driving ahead or the filtration efficiencies at cold start conditions can be investigated in future work. Furthermore, modeling of air filter efficiency and breakthrough under stationary and transient conditions will be pursued to investigate and develop advanced predictive hybrid operating strategies for road types with high local air pollution by means of simulation. Regeneration solutions, e.g., as discussed with thermal measures and a bypass line can increase the filtration robustness significantly. Realizing a purely battery-electric or fuel cell idling tunnel passage could reduce the cumulative contamination of the fuel cell stack and increase its lifetime.

4. Materials and Methods

In order to characterize and compare the performance of the various cathode filters for the fuel cell systems, a laboratory gas test bench (LGB) is used to generate synthetic gas mixtures. It was originally designed for investigations on exhaust gas after-treatment catalysts, but here adapted for the boundary conditions of fuel cell cathode air filter investigations. The entire test bench consists of three main parts: the measurement devices, the monitor and control unit, and the reactor unit. The sample, flow controller, heater, and valves are installed as shown in Figure 7. The capabilities of the test bench have already been published in several scientific works [35-37]. The temperature of the gas flow and the temperatures upstream of the filter sample are controlled by a two-stage heating system. The gas mixture of N₂, O₂, CO₂, and H₂O is heated by two preheaters via a separate line. The required total heating power is provided by a main heater. In order to avoid undesired impurities in the carrier gas nitrogen, ultrapure nitrogen 6.0 (purity higher than 99.9999%) is used for these investigations. The water and toluene required for the tests are provided via a separate vaporizing system. The fluids are stored in a tank and fed to the evaporator.

On the gas analysis side, a large number of components are measured simultaneously with a Fourier transform infrared spectrometer (FTIR) MultiGas 2030 from MKS Instruments, Inc. (Andover, MA, USA). This measurement is based on the absorption of infrared light by the individual gas components. Exhaust gas components such as water, NO, NO₂, ammonia, and toluene, which are particularly important for the present work, can be recorded with FTIR with high accuracy. From the output of the FTIR measuring device, the analysis gas is carried through a condenser to separate liquid water. Subsequently, the dry gas flow is fed into a combined measurement system, which contains a non-dispersive infrared analyzer (NDIR) for CO₂ measurement and a paramagnetic detector (PMD) for O₂ determination. A flame ionization detector (FID), which is a Thermo-FID, is used to record the total of various hydrocarbons (THC) in the analysis gas. In addition to the original setup of the test bench, further measurement devices for CO, SO₂, and H₂S are utilized to be able to conduct measurements for these species in a range between 0 and 5 ppm with a high resolution in ppb. For CO measurements, APMA-370 from Horiba Instruments is used, which is also based on non-dispersive infrared (NDIR) absorption

technology with a different calibration range. Two APSA-370 devices from Horiba Instruments enable the measurement of SO_2 and accordingly H_2S with the principle of ultraviolet fluorescence (UVF).



Figure 7. Schematic setup of the laboratory gas test bench.

Since a wide filter surface is required for the investigations, a separate sample holder is used with a diameter $d_{Filter} = 100 \text{ mm}$, as depicted in Figure 8. The synthetic gas stream can be supplied in the desired concentrations, which are regulated by different mass flow controllers (MFC) from the corresponding gas bottles. The concentrations of the different species are checked with a bypass measurement directly from the dosing unit to the measurement devices before and after each measurement to detect possible drift phenomena during measurements longer than 24 h. A type K thermocouple is placed near the tested filter to observe and control the temperature during the tests.

Three cathode air filters are selected for the investigations. The order of the individual filters is depicted in Figure 8. Both dual-layer filters have a thickness of $d_{dual-layer} = 1$ mm, whereas the thickness of the filter layers equals to $d_{triple-layer} = 5$ mm for the triple-layer filter. The clean and unused filters are preconditioned at a relative humidity of $\phi = 45\%$ and $T_{precond} = 22$ °C for at least $t_{precond,1} = 14$ h in a climate-controlled environment. After installing the test filter in the holder, it is flown through with clean air for at least $t_{precond,2} = 15$ min at the same flow rate as described in the ISO 11155-2 standard for "Road Vehicles - Air filters for passenger compartments" [38].

All filters are analyzed under the microscope and microscopic sample images with the corresponding magnification can be seen in Figure 9. All filters have a pre-filter to avoid the dust from the air. From these images, it can be observed that the active carbon filter (black) is used for each filter type as the last component from the inlet side, which enables the filtration of the most components. The particle size of the granules in the active carbon filter varies for the chosen filter types. In the SOA filter, a granule size varies from $d_{ActiveCarbon,SOA,min} = 433.9 \,\mu\text{m}$ to $d_{ActiveCarbon,SOA,max} = 1081.5 \,\mu\text{m}$, whereas the granules of the dual-layer filter are between $d_{ActiveCarbon,DL,min} = 394.1 \,\mu\text{m}$ and $d_{ActiveCarbon,DL,max} = 484.3 \,\mu\text{m}$. The granules of triple-layer vary between $d_{ActiveCarbon,TL,min} = 113.6 \,\mu\text{m}$ and $d_{ActiveCarbon,TL,max} = 593.9 \,\mu\text{m}$. The carrier material is also partially integrated into a fiber structure as seen for the NH₃-filter of the triple-layer filter. In this filter, the size of the granules can vary between

 $d_{NH_3-Filter,TL,min} = 392.8 \ \mu m$ and $d_{NH_3-Filter,TL,max} = 910.3 \ \mu m$. In conclusion, the surface of the filter can be increased with an optimized structure and there is a potential for further improvements in the filter technology for the cathode side of the fuel cells.







All investigations are carried out with a flow velocity $v_{Flow} = 0.06$ m/s, which results in a volume flow $\dot{V}_{Flow} = 28.274$ NL/s for the individual measurements. The pressure of the filter is set to p = 1.2 bar for all investigations. In order to realize realistic and comparable boundary conditions as they are expected in future applications, the temperature of the filters is set to $T_{Filter} = 40$ °C before challenging the filters with gas contamination. The air relative humidity $\phi = 50\%$ is adjusted via a water vaporizing system in advance. The duration of each measurement is determined by the filter efficiency of the sample, whereas the filter challenging is finished after reaching a filter efficiency of $\eta_{Filter} = 90\%$ or the minimum duration $t_{meas,min} = 10.000$ s. The maximum duration of one measurement takes $t_{meas,max} = 24$ h. Table 2 summarizes the gas contamination for the filter investigations. To avoid very long test durations, such as days or weeks, an accelerated stress test procedure is applied. Accordingly, concentrations are set to higher values than actually expected in air for pollutants. The concentrations of N₂, O₂, CO₂, and H₂O remain constant for all tests. For isolated investigations of the particular filters, the residual gas contamination is varied by increasing the gas concentration or by ignoring the components from the total gas matrix.

Component	Concentration	
NH ₃	60 ppm	
NO ₂	10/50 * ppm	
СО	1 ppm	
C_7H_8	80 ppm	
SO_2	1 ppm	
H_2S	1 ppm	
H ₂ O	3.64% **	
CO ₂	410 ppm	
O ₂	20.5%	
N ₂	Rest	

Table 2. Gas contamination for the filter tests at LGB.

* For the test with varying gas contamination. ** This concentration correlates to an air relative humidity of 50%.

5. Conclusions

The filtration of the air pollutant emissions in the cathodic stream plays a very important role in the aging behavior of PEM fuel cells. Within this work, different filters were investigated on a laboratory test bench in an adjustable air contamination spectrum including ammonia, nitrogen oxides, liquid hydrocarbons as well as sulfurous components. The following conclusions can be drawn from the results:

- The most dangerous sulfurous components H₂S and SO₂ for the cathode side can be filtered by all investigated filters.
- For the NOx components (NO and NO₂) only minor filtration was observed. This was
 attributed to the acid-base catalysis of the filters.
- A higher filter surface enables filtration of the hydrocarbons, as shown in the example of the toluene.
- For a successful filtration of NH₃, a further acid-coated filter is required.
- CO components in the cathodic stream cannot be filtered with the available filters.

In order to maintain a cathodic air stream without any hazardous air contamination for the cathode and the membrane, concepts with multilayered filters are necessary for the different properties of the gas molecules. Good filtration of the air contamination provides an extension of the lifetime of the fuel cell systems.

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References

- 1. Peighambardoust, S.J.; Rowshanzamir, S.; Amjadi, M. Review of the proton exchange membranes for fuel cell applications. *Int. J. Hydrogen Energy* **2010**, *35*, 9349–9384. [CrossRef]
- Ogungbemi, E.; Wilberforce, T.; Ijaodola, O.; Thompson, J.; Olabi, A. Selection of proton exchange membrane fuel cell for transportation. *Int. J. Hydrogen Energy* 2020, 46, 30625–30640. [CrossRef]
- 3. Xing, Y.H.; Li, H.; Avgouropoulos, G. Research Progress of Proton Exchange Membrane Failure and Mitigation Strategies. *Materials* **2021**, *14*, 2591. [CrossRef]
- Marcinkoski, J.; Vijayagopal, R.; Adams, J.; James, B.; Kopasz, J.; Ahluwali, R. DOE Advanced Truck Technologies. 2019. Available online: https://www.hydrogen.energy.gov/pdfs/19006_hydrogen_class8_long_haul_truck_targets.pdf (accessed on 6 August 2021).
- Zamel, N.; Li, X. Effect of contaminants on polymer electrolyte membrane fuel cells. Prog. Energy Combust. Sci. 2011, 37, 292–329. [CrossRef]
- 6. Ren, P.; Pei, P.; Li, Y.; Wu, Z.; Chen, D.; Huang, S. Degradation mechanisms of proton exchange membrane fuel cell under typical automotive operating conditions. *Prog. Energy Combust. Sci.* **2020**, *80*, 100859. [CrossRef]
- Prakash, U.; Kumar, K.; Jain, V.K. A Wavelet-based Neural Network Model to Predict Ambient Air Pollutants' Concentration. Environ. Model. Assess. 2011, 16, 503–517. [CrossRef]
- 8. Ahluwalia, R.K.; Wang, X.; Kwon, J.; Rousseau, A.; Kalinoski, J.; James, B.; Marcinkoski, J. Performance and cost of automotive fuel cell systems with ultra-low platinum loadings. *J. Power Sour.* **2011**, *16*, 503–517. [CrossRef]
- 9. Talke, A. The Influence of Selected Air Pollutants on Fuel Cells under Realistic Conditions in Vehicles. Ph.D. Thesis, The University of Duisburg-Essen, Duisburg, Germany, 16 November 2017.
- Misz, U.; Burfeind, J.; Beckhaus, P.; Heinzel, A. Analysis of the Influence of a Filter for Trafic-Related Gaseous and Chaptericulate Contaminants on PEMFC. In *Essen Schriften des Forschungszentrums Jülich / Energy & Environment*; Institute of Energy Research-Fuel Cells (IEF-3) Forschungszentrum Jülich GmbH: Jülich, Germany, 2010; ISBN 78-3-89336-651-4.
- 11. Mohtadi, R.; Lee, W.-k.; Zee, J.W.v. Assessing durability of cathodes exposed to common air impurities. *J. Power Sources* 2004, 138, 216–225. [CrossRef]
- 12. Lopes, T.; Sansinena, J.-M.; Mukundan, R.H.D.S.; Jacobson, D.L.; Garzon, F.H. Diagnosing the Effects of Ammonia Exposure on PEFC Cathodes. *J. Electrochem. Soc.* 2014, *161*, F703. [CrossRef]
- Talke, A.; Misz, U.; Konrad, G.; Heinzel, A. Impact of Air Contaminants on Subscale Single Fuel Cells and an Automotive Short Stack. J. Electr. Eng. 2015, 3, 70–79.
- 14. Talke, A.; Misz, U.; Konrad, G.; Heinzel, A.; Klemp, D.; Wegener, R. Influence of urban air on proton exchange membrane fuel cell vehicles—Long term effects of air contaminants in an authentic driving cycle. *J. Power Sour.* **2018**, 400, 556–565. [CrossRef]
- 15. European Standards. ISO 14687:2019 Hydrogen Fuel Quality—Product Specification; Beuth Verlag GmbH: Berlin, Germany, 2019.
- 16. Hydrogen Fuel Quality for Fuel Cell Vehicles; SAE International: Warrendale, PA, USA, 2011.
- 17. Klemp, D.; Wegner, R. Forschungszentrum Jülich MOBILAB. Available online: https://www.fz-juelich.de/iek/iek-8/EN/ Expertise/Infrastructure/MobiLab/MobiLab_node.html (accessed on 29 October 2021).
- 18. Cheng, X.; Shi, Z.; Glass, N.; Zhang, L.; Zhang, J.; Song, D.; Liu, Z.-S.; Wang, H.; Shen, J. A review of PEM hydrogen fuel cell contamination: Impacts, mechanisms and mitigation. *J. Power Sour.* **2007**, *165*, 739–756. [CrossRef]
- 19. Bruijn, F.A.d.; Dam, V.A.T.; Janssen, G.J.M. Review: Durability and Degradation Issues of PEM Fuel Cell Components. *Fuel Cells* 2008, *8*, 3–22. [CrossRef]
- 20. Baturina, O.; Dyatkin, B.; Reshetenko, T. *Influence of Air Impurities on the Performance of Nanostructured PEMFC Catalysts*; Springer: Berlin/Heidelberg, Germany, 2018.
- EMCEL. Wie Wirkt Sich Wasserstoffverunreinigung Auf Eine Brennstoffzelle Aus? 2018. Available online: https://emcel.com/ de/wasserstoffverunreinigung-in-brennstoffzellen/ (accessed on 26 July 2021).
- Wang, L.; Zhou, Y.; Yang, Y.; Subramanian, A.; Kisslinger, K.; Zuo, X.; Chuang, Y.-C.; Yin, Y.; Nam, C.-Y.; Rafailovich, M.H. Suppression of Carbon Monoxide Poisoning in Proton Exchange Membrane Fuel Cells via Gold Nanoparticle/Titania Ultrathin Film Heterogeneous Catalysts. *Appl. Ener. Mater.* 2019, 2, 3479–3487. [CrossRef]
- 23. Jiménez, S.; Soler, J.; Valenzuela, R.; Daza, L. Assessment of the performance of a PEMFC in the presence of CO. *J. Power Sources* 2005, 151, 69–73. [CrossRef]
- 24. Tullius, V.; Zobel, M.; Dyck, A. Development of a Heuristic Control Algorithm for Detection and Regeneration of CO Poisoned LT-PEMFC Stacks in Stationary Applications. *Energies* **2020**, *13*, 4648. [CrossRef]
- 25. Misz, U.; Talke, A.; Heinzel, A.; Konrad, G. Sensitivity Analyses on the Impact of Air Contaminants on Automotive Fuel Cells. *Fuel Cells* **2016**, *16*, 444–462. [CrossRef]
- 26. Misz, U.; Talke, A.; Heinzel, A.; Beckhaus, P. Effects, Damage Characteristics and Recovery Potential of Traffic-induced Nitric Oxide Emissions in PEM Fuel Cells under Variable Operating Conditions. *Fuel Cells* **2018**, *18*, 594–601. [CrossRef]
- Talke, A.; Misz, U.; Konrad, G.; Heinzel, A. Influence of Nitrogen Compounds on PEMFC: A Comparative Study. J. Electrochem. Soc. 2018, 165, F3111. [CrossRef]
- 28. Chen, M.; Du, C.; Zhang, J.; Wang, P.; Zhu, T. Effect, mechanism and recovery of nitrogen oxides poisoning on oxygen reduction reaction at Pt/C catalysts. *J. Power Sources* **2011**, *196*, 620–626. [CrossRef]

- 29. Tsushima, S.; Kaneko, K.; Hirai, S. Two-Stage Degradation of PEMFC Performance due to Sulfur Dioxide Contamination; The Electrochemical Society: Pennington, NJ, USA, 2010.
- 30. Kaneko, K.; Tsushima, S.; Hirai, S. *Effect of SO*₂ *Concentration and Relative Humidity on Contamination of Cathode and Anode in PEMFC*; The Electrochemical Society: Pennington, NJ, USA, 2009.
- 31. Punyawudho, K.; Monnier, J.; Zee, J.W.V. SO2 Adsorption on Carbon-Supported Pt Electrocatalysts; The Electrochemical Society: Pennington, NJ, USA, 2009.
- 32. El-Deab, M.; Kitamura, F.; Ohsaka, T. Poisoning Effect of Selected Hydrocarbon Impurities on the Catalytic Performance of Pt/C Catalysts towards the Oxygen Reduction Reaction; The Electrochemical Society: Pennington, NJ, USA, 2013.
- Kätzel, J.; Markötter, H.; Arlt, T.; Klages, M.; Haussmann, J.; Messerschmidt, M.; Kardjilov, N.; Scholta, J.; Banhart, J.; Manke, I. Effect of Ageing of Gas Diffusion Layers on the Water Distribution in Flow Field Channels of Polymer Electrolyte Membrane Fuel Cells. J. Power Sour. 2016, 301, 386–391. [CrossRef]
- Li, H.; Zhang, J.; Shi, Z.; Song, D.; Fatih, K.; Wu, S.; Wang, H.; Zhang, J.; Jia, N.; Wessel, S. PEM Fuel Cell Contamination: Effects of Operating Conditions on Toluene-Induced Cathode Degradation; The Electrochemical Society: Pennington, NJ, USA, 2008.
- 35. Holderbaum, B.; Laible, T.; Pischinger, S. Internal and External Measures for Catalyst Light-Off Support; SAE International: Warrendale, NJ, USA, 2015.
- Schönebaum, S.; Dornseiffer, J.; Mauermann, P.; Wolkenar, B.; Sterlepper, S.; Wessel, E.; Iskandar, R.; Mayer, J.; Weirich, T.; Pischinger, S.; et al. Composition/Performance Evaluation of Lean NOx Trap Catalysts for Coupling with SCR Technology. *Chem. Cat. Chem.* 2021, *13*, 1787–1805; [CrossRef]
- 37. Wolkenar, B.; Schönebaum, S.; Mauermann, P.; Dittmann, P.; Pischinger, S.; Simon, U. Storage and Oxidation of Oxygen-Free and Oxygenated Hydrocarbons on a Pt–Pd Series Production Oxidation Catalyst. *Top. Catal.* **2019**, *62*, 376–385. [CrossRef]
- 38. European Standards. ISO 11155-2 Road Vehicles—Air Filters for Passenger Compartments—Part. 2: Test. for Gaseous Filtration; Beuth Verlag GmbH: Berlin, Germany, 2009.