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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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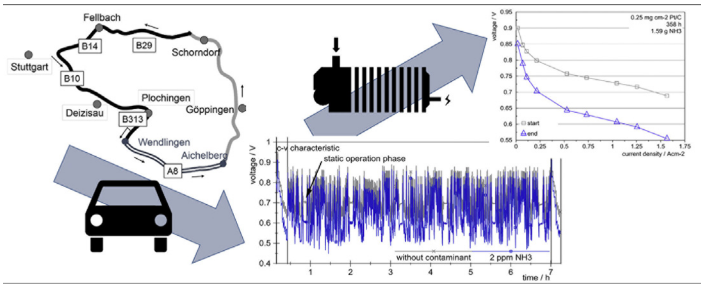
HIGHLIGHTS

- 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