EVS30 Symposium
Stuttgart, Germany, October 9 - 11, 2017

Contamination Control for Fuel Cell Systems

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Summary

Fuel cell technology has reached technical maturity, yet significant system cost reductions must be achieved to reach market penetration without sacrificing durability and robustness. Cost-effective Contamination Control solutions to reduce degradation in the cooling loop and cathode air path have been developed. Research on the sensitivity of a polymer electrolyte membrane (PEM) fuel cell against airborne contamination in the laboratory, followed by real-life evaluations, led to the development of adsorbents for cathode air filters tailored to effective protection. In addition, innovative design options offer cost-balanced solutions for a wide range of applications. To prevent the fuel cell system from corrosion and electric shorts, ion exchange resins have been qualified to keep the electric conductivity and ion contamination in the liquid cooling circuit low.

Keywords: Component, Cooling, PEM fuel cell, Fuel cell vehicle, Pollution

1 Motivation

Climate change is one of the major threats to mankind. To reach the target of maximum 1.5°C temperature rise compared to pre-industrial levels set by the COP21 Conference in Paris[1], emissions from transport, accounting for 23% of the total CO_2 emissions[2], have to be drastically reduced. Whereas Battery Electric Vehicles (BEV) using Li ion batteries are limited in power density and capacity, Fuel Cell Electric Vehicles (FCEV) offer driving ranges and fueling comparable to today´s Internal Combustion Engine (ICE) vehicles.

Lowering system cost and improving system lifetime by limiting degradation are essential for the market success of LT PEM Fuel Cell technology. The following chapters will highlight solutions for this challenge.

2 Strategic Approach

As the current worldwide production volume of FCEVs is still low, it is beneficial to develop market products for the low temperature-PEM (LT-PEM) technology that can be used for non-automotive early markets as well. The basis for effective system protection is an in-depth understanding of the negative effects of real-life contaminants on fuel cell durability. Filtration and separation materials have to be developed to specifically target the most harmful contaminations for all relevant applications, e.g. micro combined head and power (µ-CHP) installations, forklifts and passenger cars.

To be able to achieve product cost reductions, standardized, yet flexible product designs are needed. This enables volume bundling, helping to keep development and tooling costs low. Concepts enabling fast adaptions to concrete applications are a prerequisite for this approach.

3 Cathode Air Filter

3.1 Problem description

3.1.1 Laboratory investigation

Gaseous contaminations in the cathode air have a negative impact on the durability of LT PEM Fuel Cell Systems, e.g. through poisoning of the Platinum catalyst or damaging of the membrane. The sensitivity of the cell voltage is expected to increase as Platinum loading must be reduced to achieve cost savings. In a publically funded project[3], the main sources for degradation were identified systematically. Gases containing S- and N- atoms like SO_2, NO_x turned out to be especially harmful to the system performance. Particles, e.g. salt crystals, also have a negative impact and have to be separated (figure1). The presence of ammonia at concentration levels as low as 1 ppm poisons the electrodes of the cell which in turn affects the cell voltage[4] as well.

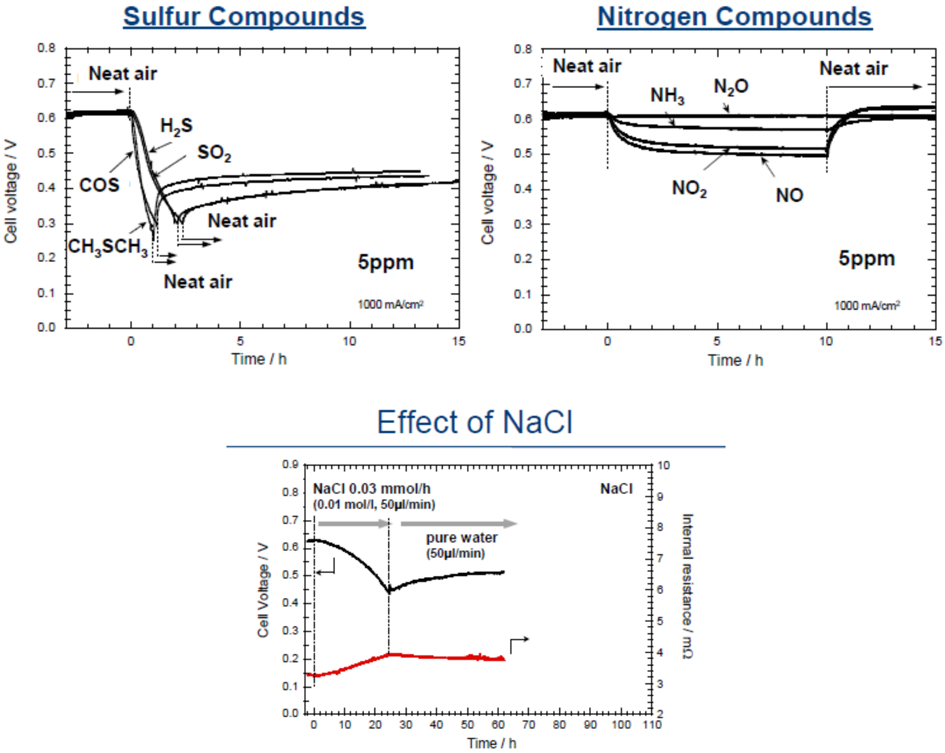


Figure1: Laboratory tests of effect from contamination on fuel cell voltage[5]

Poisoning the cathode with different gases showed that the pollutants could cause a significant performance drop, which partly is irreversible without an active recovering. Further investigations showed that the critical concentration level for an impact on the cell voltage can be quite low. Beside the harmful gases a negative effect of ions, originating from salt particles like NaCl, negatively affect the cell voltage as well. The risk of such a contamination is especially high in coastal areas[5].

3.1.2 Real-life contamination

The validation of the relevance of these laboratory results is the target of several public funded projects. The positive effect of adsorptive filter elements on fuel cell degradation was shown under real-life conditions. In a stationary fuel cell system containing two short-stacks, one stack was run without a filter element while a cathode air filter protected the other stack. Both started at the same cell voltage. As shown in figure 2, the degradation of the unprotected cell was more severe. In addition, with continuous gas measurements it could be shown, that NO_X has a direct influence on the cell voltage under real-life conditions as well. The detected peaks of the pollutant directly lead to a partly reversible voltage drop of the fuel cell. The reaction of the filter-protected cell is much less pronounced which proves the functionality of the adsorptive cathode air filter.

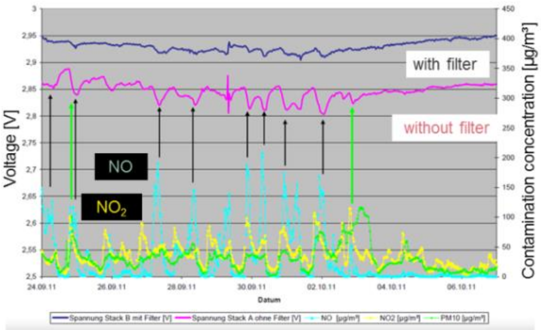
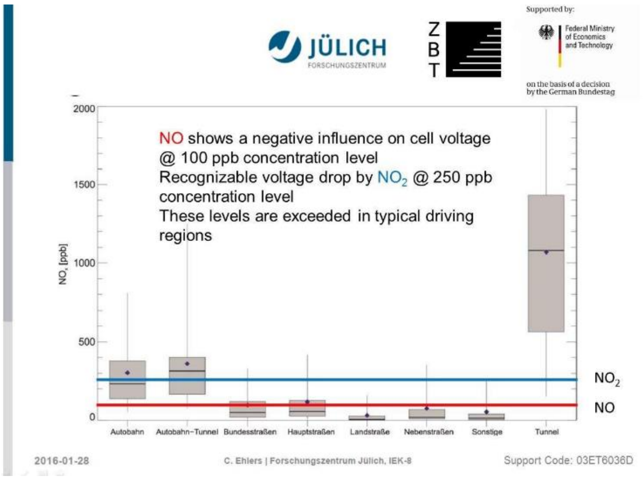


Figure2: Filter performance under real-life conditions[3]

One of the targets of the publically funded project ALASKA (Auswertung von Luftschadstoffszenarien zur Auslegung von Schadgasfiltern und Kathodenregenerationszyklen für Automotiv-Brennstoffzellen) is to continue the development of adsorbents against gases poisoning the fuel cell and to gain a better understanding of the needed capacity and lifetime of a filter, with a special focus on the effect of peak concentrations. Therefore, a truck equipped with several analysers for the designated harmful gases operated as a mobile lab, measuring the concentration of the harmful substances in different road areas with highly resolution in time. After a statistically relevant number of measurements, the spectrum of harmful substances could be related to the different types of roads (figure3). By using well-investigated driver profiles, the requirement for protection for different drive cases could be created and led to a knowledge-based development of the cathode air filter. Furthermore, the highly sensitive test equipment can be used to investigate the behaviour of the adsorbent under real-life condition to achieve additional improvement.



NO shows a negative influence on cell voltage @ 100 ppb concentration level

Recognizable voltage drop by NO_2 @ 250 ppb concentration level

These levels are exceeded in typical driving regions

Figure3: Real live NO_X Pollution over different road types[6]

3.2 Materials and product design features

3.2.1 Activated carbon development

Based on the environmental conditions collected in projects like ALAKSA, the development of adsorbents can be enforced to yield different selectivities. Activated carbons showcase a series of advantages that makes them a suitable adsorbent choice. Considering polar gases as adsorption targets, the possibility of tailoring the porous structure and surface chemistry by way of activation and impregnation, enable ammonia or NO_x removal[7]. Since activated carbons mostly possess non-polar groups on their surfaces, acid impregnation is important for adsorbing polar gases such as ammonia or NO_x. For sulfur compounds, a catalytic modification improves the performance of the activated carbon, due to its support of the following reactions.

$$H_2S + 2\ O_2 \rightarrow H_2SO_4 \qquad (1)$$

$$\begin{gathered} SO_2 + \tfrac{1}{2}\ O_2 \rightarrow SO_3 \\ SO_3 + H_2O \rightarrow H_2SO_4 \end{gathered} \qquad (2)^8$$

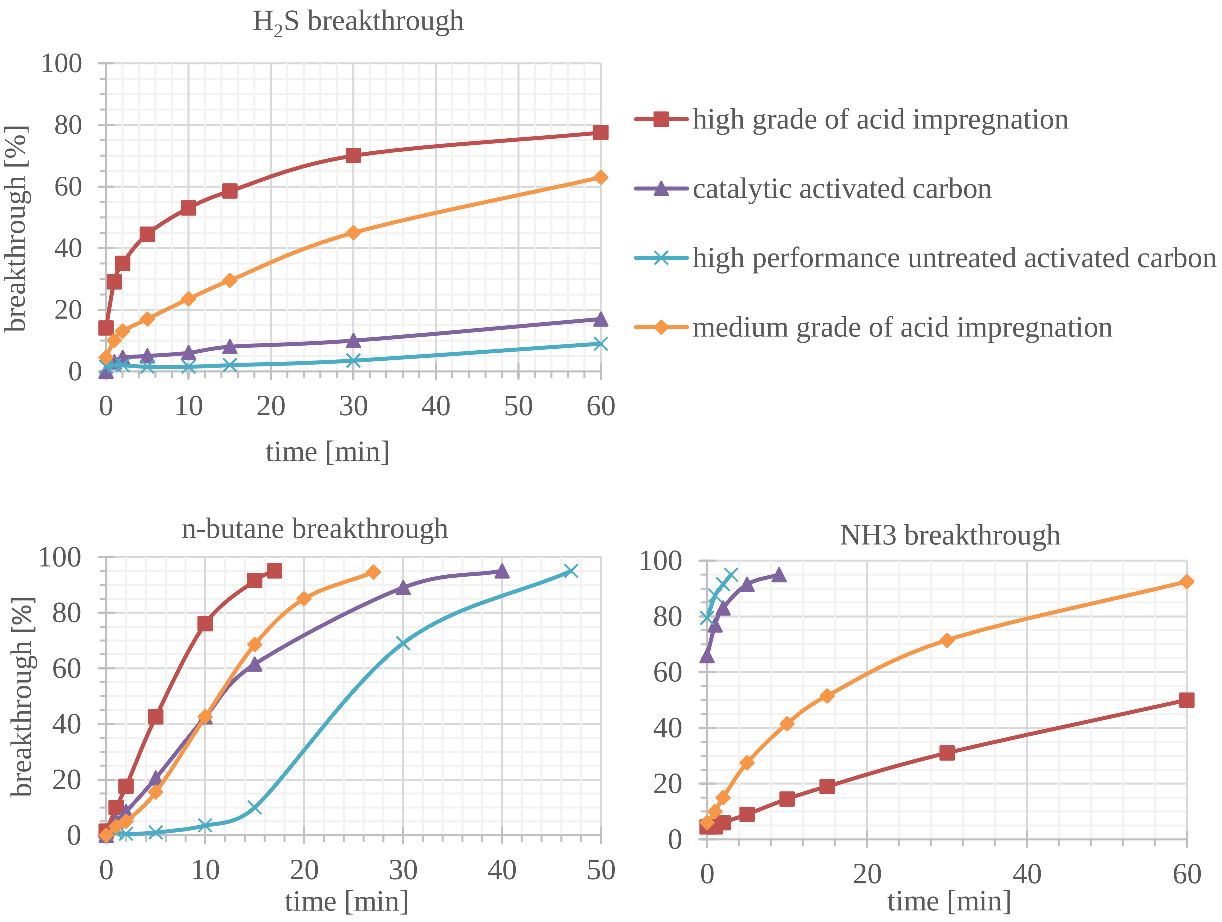


Figure4: Breakthrough profiles for different activated carbons

3.2.2 Media development

3.2.2.1 Adsorbent materials

Bulk measurements (figure 4) of *different* activated carbon types showed that different treatments are beneficial for some characteristic groups but lead to a performance drop for other substances. Additionally the separation efficiency for some gases can be lower if other, more strongly bonding molecules are present in gas mixtures. As shown in Cap 3.1.1, protection against a broad range of harmful substances is required. Real-life measurements display that those pollutants are present in the environment in relevant concentrations (Cap 3.1.2). Therefore, further research led to the development of multilayer media containing these tailored adsorbents in the different layers.

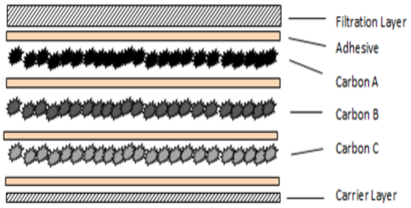
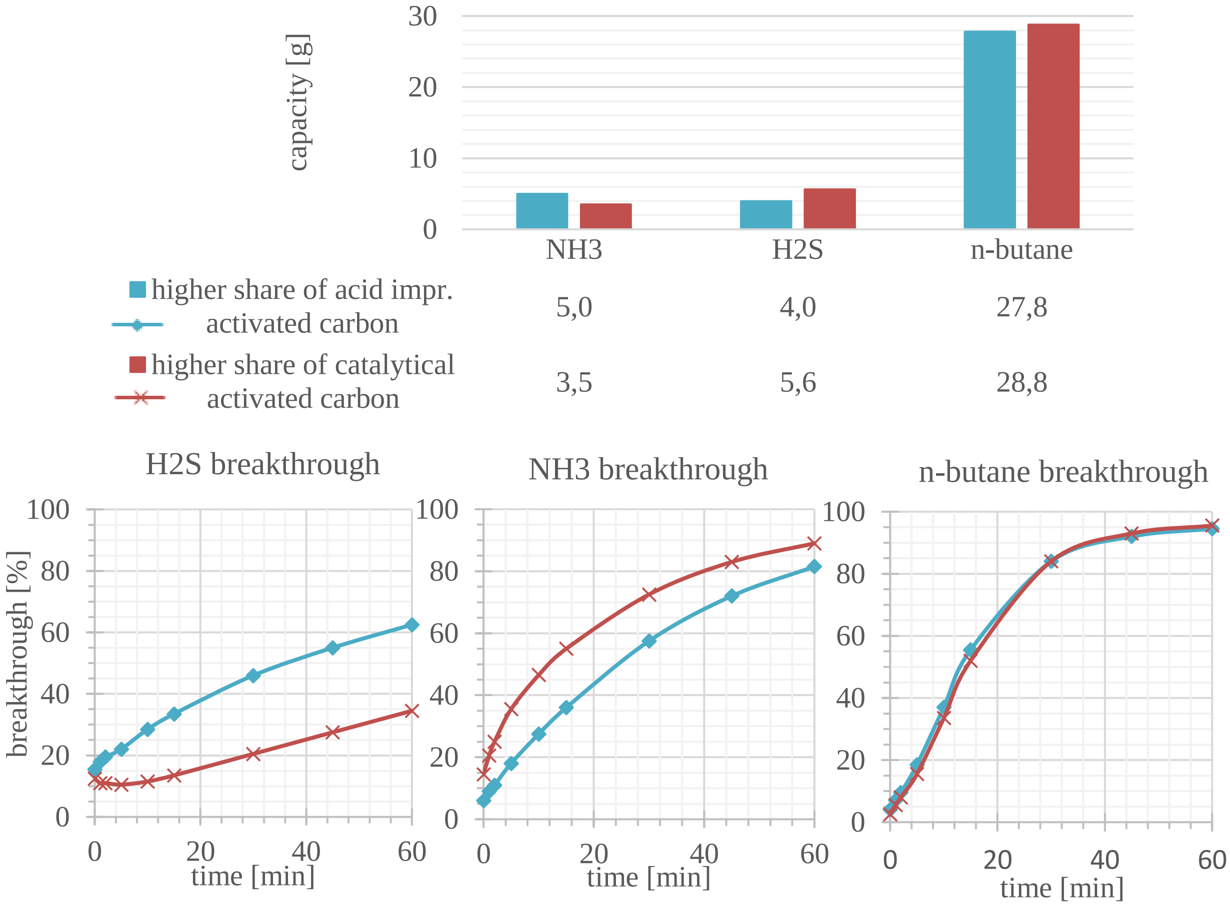


Figure5: Multilayer design for gas mixtures

By selection of the most specific activated carbons and mixing them in the right proportion, the performance range of the adsorption media could be optimized to the demand of the pollution in the environment. If the systems should run in areas with a high sulphur pollution like volcanic areas, the share of catalytic activated carbon should be higher. For ammonia-polluted regions, a media with a higher content of the activated carbon with an acid impregnation led to more capacity. Through this, multilayer media can be easily tailored for specific requirements.



	NH3	H2S	n-butane
higher share of acid impr. activated carbon	5,0	4,0	27,8
higher share of catalytical activated carbon	3,5	5,6	28,8

Figure6: Breakthrough and capacity measurements on filter media

Figure 6 shows the results of such media compositions. By using a higher share of the acid-impregnated carbon, the NH_3 adsorption capacity could be increased, resulting in a decrease of SO_2 adsorption capacity. The same is applicable vice versa. Special care has to be taken of the right sequence of layers for full adsorption performance. Very selective adsorbent should be placed on the upstream side so that the pollutants don't block the capacity of the less specific ones.

3.2.2.2 Particle filter media

As described in chapter 3.1.1 salt particles can drain the cell voltage as well. High efficiency particulate air (HEPA) media according to EN1822 show particle separation efficiencies of 99.95 % at the most penetrating particle size. Therefore, such a media protects the cathode against NaCl particles very well. The disadvantage is a potentially fast media clogging, which requires a pre filter in a dusty environment. To avoid an extended demand of mounting space, a double layer bellow was developed.

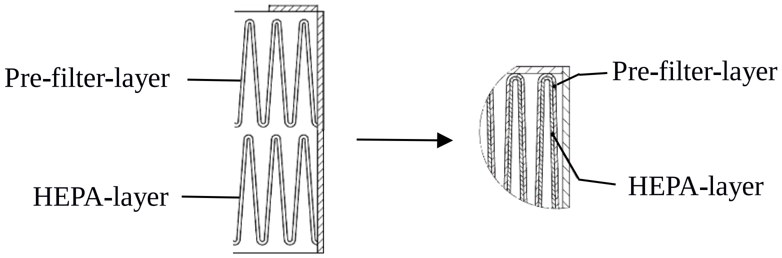


Figure7: Double layer bellow

Here a HEPA media layer is pleated together with a media having a lower efficiency and a higher dust holding capacity. In this structure it is possible to generate a safe protection against fine particles as well as a sufficient dust holding capacity in a minimum mounting space.

3.2.3 Filter Designs

Laminated activated carbon media offer the advantage that the adsorbent is fixed in a position without any influence from movement or vibrations of the system. Furthermore, the pressure drop could be optimized in relation to the performance density of the activated carbon with different design concepts. The trade-off between the performance characteristics (separation efficiency, capacity and pressure loss) on filter element level led to the development of three standardized filter element design options enabling cost savings for best compromise between packaging constraints and adsorption performance (figure8).

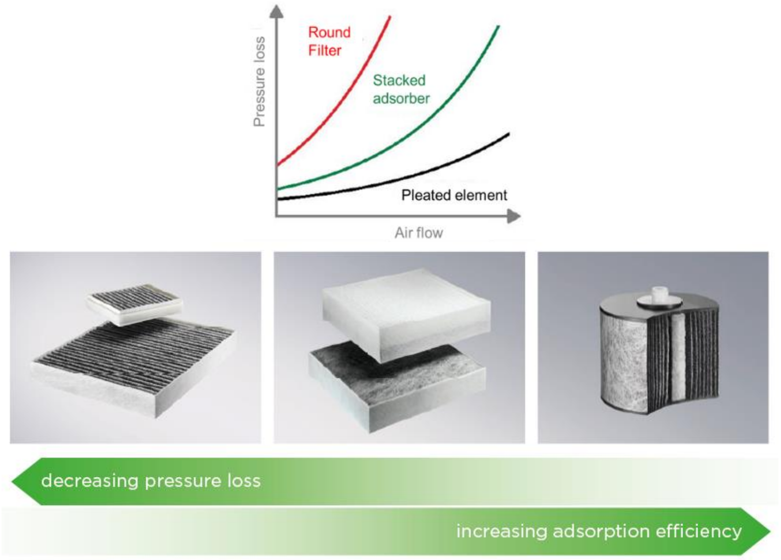


Figure8: Design concepts

A standard pleated filter brings the benefit of a high filtration surface which leads to a lower media velocity and a low pressure drop, especially important for high volume flows, e.g. in FCEV. The open structure of a pleated filter results in of a lower performance density. Alternatively, a stacked filter can be applied to gain a higher utilization of the available mounting space. The higher amount of activated carbon in the same volume brings more capacity and a longer contact time with the adsorbent. The higher carbon and performance density leads to a higher pressure loss of the filter element. In addition, a wrapped filter design was developed. In fuel cell systems the air is often supplied through tubes or hoses to which the wrapped filter can be directly adapted to. This makes housing obsolete, helping to reduce system costs. Additionally this f-cell awarded[9] round filter design could adapted quite easy to the customer demand in terms of height, diameter and connection solution. First tests in customer corporations using solid oxide fuel cell (SOFC) systems showed a positive effect on the degradation of the cell voltage as well. This opens the door to new market segments enabling volume bundling for further cost reduction.

4 Ion Exchange Filter

4.1 Problem description

To remove the heat generated by the fuel cell stack, liquid cooling with water-glycol mixtures is often used. It is crucial to keep the liquid at a very low conductivity to avoid electrical shorts in the fuel cell stack. During operation, ions can enter the liquid e.g. from metal surfaces of coolant loop components, additives from plastics, and corrosion, leading to an increase in conductivity. Furthermore, corrosion caused by those reactive ions in the cooling circuit is observed. Deposits containing different metal ions (Cr, Mn, Fe, Ni and Ca) indicate a degradation of the material´s surfaces which can harm the fuel cell additionally (figure9). H_2O_2 can be formed in the fuel cell and even if the membrane is resistant against it under normal conditions, the presence of metal ions together with H_2O_2 will catalyse the chemical degradation of the membrane. Additionally, almost all cations (except Li^+) can replace the protons in the sulfonic acid functions of the membrane, which leads to a decreased protonic conductivity and therefore a performance drop[10]. To keep the conductivity low and to protect the coolant loop from accelerated corrosion, ion exchange technology is applied.

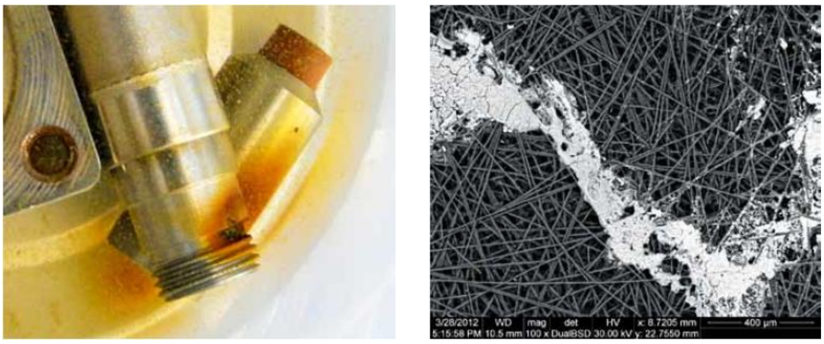


Figure9: (l.) Corroded vents in DI-Water (r.) deposits of metal ions[10]

4.2 Materials and product design

A mixture of strongly acidic and basic resins was developed which maintain their high volumetric capacity even at elevated temperatures, enabling their use in automotive applications. Strongly basic ion exchange resins often show a loss of capacity caused by thermal degradation of the functional groups. This effect is attributed to the “Hofmann Degradation” which eliminates one Methyl group from the quarternary functional group, yielding a tertiary amine, or even eliminates the whole functional group. Both mechanisms require the presence of OH^--anions. For thermal aging tests, the resins where immersed in a water / ethylene glycol mixture and stored for three weeks at 90°C. The samples´ remaining ion exchange capacity were measured and compared to the initial values, showing the degree of temperature-induced degradation. Monodisperse polystyrene-divinylbenzene (PS-DVB) copolymer resins with sulfonic acid and quaternary Ammonium functions combined good volume-based capacity with a very low degradation after the aging procedure.

To achieve full utilization of the resin mix, an innovative grid structure was developed. The internal lattice structure directs the coolant flow in a way that all resin is used efficiently. In addition, the internal matrix structure keeps the resin beads from tightly packing and therefore lowering the pressure loss in operation. The internal structure also stops resin de-mixing caused by vibration in fuel cell systems (Figure 10).

Figure10: Homogenous flow field at Ion Exchange Filter inlet

As the levels of ionic contamination and drag-in rates were not known, typical contamination levels, main contaminants and drag-in rates were defined based on literature research for proof-of-concept testing. The fulfilment of the separation task was demonstrated (figure11). The qualification of the service interval depends on the unique application and is done together with the customer, based on field experience.

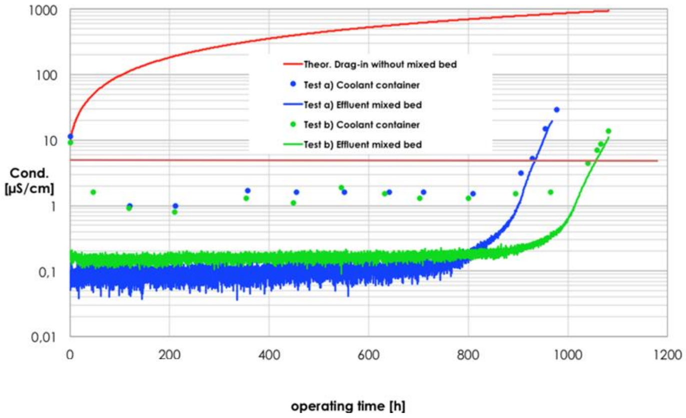


Figure11: Breakthrough curve of an Ion Exchange Filter

Additional tests showed that the material is also well-suited to keep the conductivity of water-methanol mix used in direct methanol fuel cell (DMFC) low. As a first test, the leaching performance was analysed, showing the stability of the resins under the typical operating conditions. Testing the resin´s ion exchange capacity in a water-methanol mixture showed a very good volume-specific capacity and system protection (Figure 12)[11], which offers new applications.

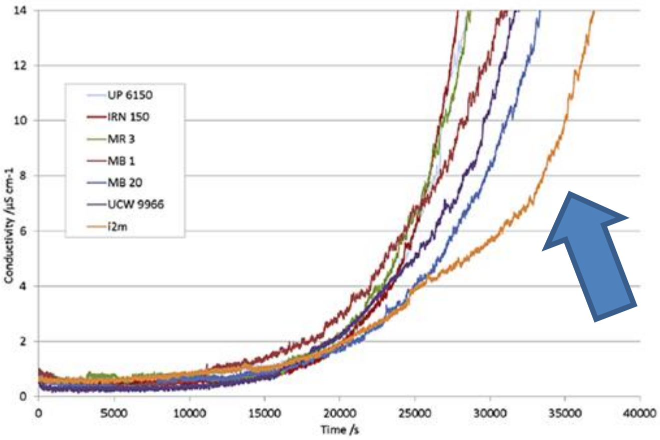


Figure12: Conductivity vs. time for different ion exchange resin (IER) materials[11]

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