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Impact of hydrogen impurities measured on PEMFC stacks in conditions representative of the automotive application.

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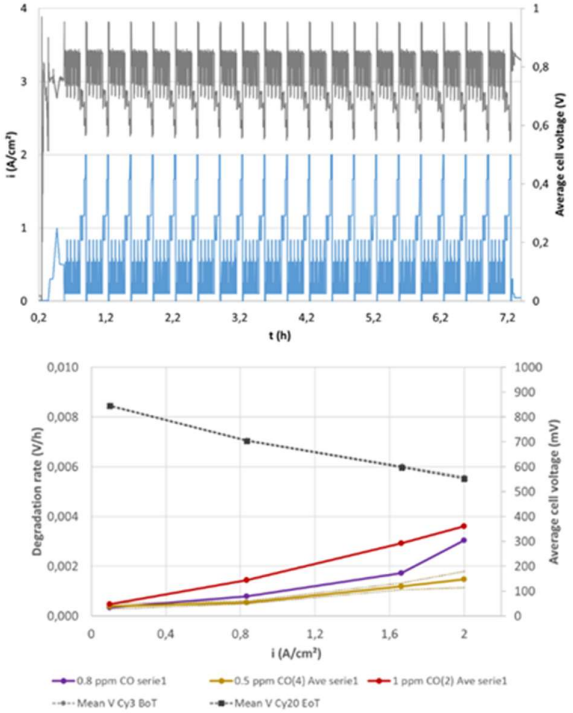
Proton Exchange Membrane Fuel Cell (PEMFC) technologies are considered as a promising and clean energy supply for both transportation and stationary applications. State of art components present performance enabling integration of stacks in actual systems and vehicles. However, several improvements are still needed to enable largescale competitive deployment such as better lifetime, lower cost, and overall upgraded reliability including tolerance to all conditions imposed by the applications such as the tolerance to impurities potentially present in the air or in the hydrogen.

In HYDRAITE project, the impact of different impurities present in the hydrogen when coming out from the hydrogen refueling station (HRS) into the fuel cell (FC) car are measured. Measurements were conducted on the PowerCell stacks. Different impurities were considered and studied by the consortium following relevant protocols as described in several public reports available on the webpage [1]. The following impurities were those considered in the experiments conducted at CEA presented here: CO as the main reversible impurity, H_2S as the main non-reversible one with also its impact onto CO tolerance, and also toluene as selected for tests on stacks among new impurities identified from analyses at HRS. To assess impact of impurities in conditions as near as possible to real operation of the stacks within a PEMFC system, test bench is adapted with a recirculation loop to enable efficient use of hydrogen and possible accumulation effect. In addition, gas analyzers are implemented to analyze and get concentrations of different gases of interest within the fuel line, such as gases coming from the cathode side or hydrogen impurities.

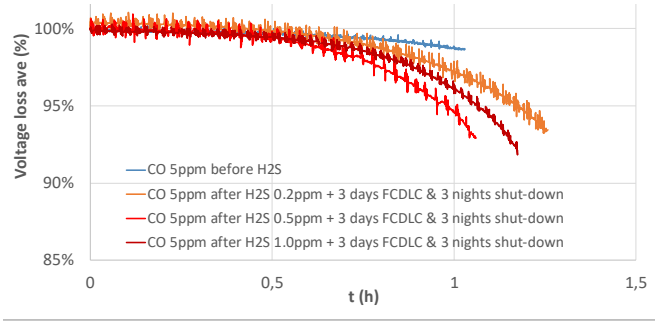
For the experiments presented here, the following type of test program was applied as originally defined for the project: HYDRAITE start-up and break-in procedures are applied with a first step under nitrogen to increase temperature, then a switch to active gases when reaching 45°C, application of a predetermined current profile including operation at a nominal current, then few minutes at low current density (also corresponding to the minimum flow rates) and few minutes at the highest current density applicable (normally also corresponding to the maximum load during the polarization curves and during the dynamic load cycles. After conditioning, the reference tests include a polarization curve under pure hydrogen and a CO tolerance test conducted with 5 ppm CO at fixed current density (corresponding to about 0.7 V). Both reference measurements aim at monitoring the status of the stack before and after series of poisoning tests, allowing to determine if and how the performance of the MEAs under pure hydrogen and the tolerance of the MEAs are affected.



The protocols and poisoning tests under Fuel Cell Dynamic Load Cycles (FC-DLC) following Stacktest recommendations [2] are conducted over one day to better mimic operation of a car on maximum a daily period. This allowed applying 20 cycles, the two first ones being always under pure Hydrogen.

The results reported (Figure 1) are giving example from tests conducted with the stacks S2 (191 cm²) and S3 (300 cm²) designs commercialized by PowerCell, the latter being the follow-up of the stack developed within the project AutoStackCore. Impact of carbon monoxide was assessed for concentrations below 1 ppm under FC-DLC applied during daily experiments. The two stacks showed same trends considering the effect of CO concentration, with a confirmed negative impact on daily performance losses during FC-DLC tests caused by increasing the CO concentration at more than 0.5 ppm, as measured with 0.8 and 1ppm. The S3 stack showed in general lower sensitivity to same type of dynamic load cycles (in terms of induced voltage cycles) and to CO contamination. This better behavior can be attributed to differences in the membrane electrodes assemblies' composition and in the local conditions induced by operating features, which are both adapted in purpose to reach better performance.

Figure 1. Example of current density and average cell voltage during one day of FC-DLC experiment on a S3 stack (top). Average cell voltage and daily degradation rates under FC-DLC with 0.5, 0.8 and 1 ppm CO vs. current density (bottom).



Other test campaigns were conducted to check the impact of a contamination by H_2S, for various concentrations (0.2, 0.5 and 1 ppm). Protocols started with contamination by H_2S at fixed current density (0.3 A/cm²), then applying 5 ppm CO tolerance test, then trying recovery by successive days of DLC and overnight shutdowns (Figure 2). For all cases, some recovery could be demonstrated regarding CO tolerance thanks to 4 overnight shutdowns and 3 days of dynamic load cycles but total reversibility could not be obtained.

Figure 2. Comparison of voltage decrease in % of initial value during CO 5 ppm tolerance tests just after contamination with H_2S from 0.2 ppm to 1ppm and after recovery by cycling under FC-DLC and overnight shut-downs (x3).

In addition to voltage and current measurements, gas analyses were conducted by sampling fuel from the recirculation loop to get the concentrations in nitrogen, argon, oxygen (in %) and carbon dioxide (in ppm) measured by a µGC, and concentrations in methane, carbon monoxide or hydrogen sulfide measured by IR-laser with a Proceas. Data reported (Figure 3) showed the % of nitrogen coming by permeation through the membrane from the air feeding the cathode, like for the argon. These data, particularly the percentage of N_2 in the range of 8 to 12% indicate that the fuel-feeding mode with recirculation, purges and a flow limiter is consistent with actual use of a stack within a system. Argon data seem consistent with the concentration of argon generally estimated for air composition. On the contrary, oxygen could not be detected whereas few % are also supposed to permeate through the membrane (referring to air composition even while of course taking into account consumption by oxygen reduction at the cathode): this is attributed to the possible reactions involving oxygen in the presence of hydrogen and catalyst. Of course, the aim was to check differences in O_2 concentration when CO is added, considering their reaction for CO_2 formation but this could not be evidenced in our case, probably due a detection limit higher than needed. CO_2 can also be mainly coming from the air (variations with time seems consistent with observations done in parallel on the composition of the ambient air used here) and partly from the hydrogen, or from reactions involving CO or the carbon support anode side. Measurements also indicated that some CH_4 is always present in the hydrogen storage used, then reaching by accumulation after few hours of cycles concentrations of few ppm. CO measurements within the gas circulating in the loop give values below the impurity concentration provided from the tanks, about 10% in the higher cases, thus confirming strong adsorption.

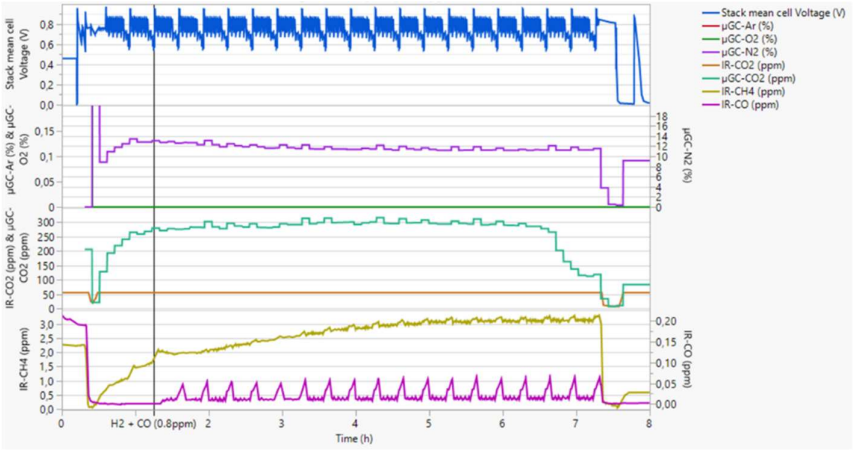


Figure 3. stack average cell voltage during FC-DLC and concentrations in nitrogen, argon, oxygen (in %), carbone dioxide (in ppm), methane and carbon monoxide conducted by sampling fuel from the recirculation loop.

During the contamination tests by H_2S and CO poisoning, analyses could also be conducted at the stack outlet. Results showed that the voltage loss of respectively 30 or 50 mV indeed correspond to a coverage state just before an adsorption threshold is reached, as shown by the increase of H_2S and CO measured at these moments. Maximum concentrations measured of about 16% of injected concentration for H_2S and again about 10% for CO confirmed their strong adsorption.

Acknowledgements

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[1] https://hydraite.eu/public-reports/
[2] http://stacktest.zsw-bw.de