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H_2FC

Integrating European Infrastructure to support science and development of Hydrogen- and Fuel Cell Technologies towards European Strategy for Sustainable, Competitive and Secure Energy

Deliverable 8.8

D8.8 Test Rig for Fuel Quality and Fuel Type System Testing

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Contributing partners (short names)	**VTT, Juelich**

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Document History

Issue Date	Version	Changes Made/Comments
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Introduction

The Deliverable 8.8 - Test Rig for Fuel Quality and Fuel Type System Testing - is referred to the subtask JRA2.5.2 of WP8. The task title is “Test facilities for HT FC multi fuel feeding and poisoning”, described as follows:

- The aim is the analysis of the history of the functional and ambient operating conditions and the corresponding performance trend of the system under study, for the development of expert system for the on-line evaluation of the system health status and residual life. The impact of this task is the development of management and control tools of the facilities to schedule suitable life cycle tests with operating conditions variation and the monitoring of all the characteristic parameters

During the activity the three partners involved shared research information and realized facility upgrades for multi feeding and poisoning. The result is an infrastructure unique and coordinated that permits offer to externals in transnational access (TNA) a unique infrastructure in terms of test typology and in terms of shared methods and procedures between H2FC partners. This latter enhances also cooperation between partners in the all join research activity (e.g. standardization and modelling).The deliverable was competed 100% at M24.

Description of the experimental infrastructure and of the points to be improved

The activity was focused since the beginning on the effect of contaminants in the fuel inlet. Especially fuel gas generated from renewable sources generally contains various contaminants. The concentration of these contaminants strongly depends on the source of the fuel. Fuels from digestive generation contain high concentrations of ammonia and sulfur containing compounds. Gases from gasification generally contain higher concentrations of tar and dust. The influence of these contaminants on the performance of SOFC single cells have been studied in the Forschungszentrum Jülich in various projects mainly focusing on fuels from coal and lignite gasification. The various contaminants have been classified and representative compounds were selected to simulate the contaminated fuel gas. The compounds were tested separately so no cross influences were studied. The duration of the exposure of the SOFC cells to the contaminant varied. In figure the studied components and the concentration in the fuel gas are listed.

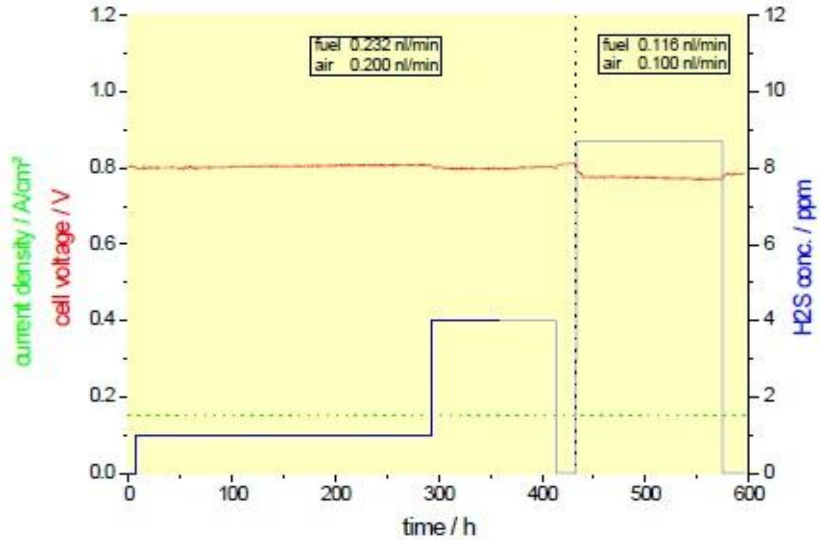
Unsaturated Hydrocarbons				
C2H4	7 ppm	100 h	950 °C	ESC
Gaseous				
NH3	4800 ppm	101 h	950 °C	ESC
HCN	5 ppm	525 h	800 °C	ASC
	10 ppm	650 h	800 °C	ASC
	20 ppm	856 h	800 °C	ASC
	200 ppm	130 h	950 °C	ESC
HCl	5 ppm	50 h	800 °C	
H2S	1 ppm	292 h	950 °C	ESC
	4 ppm	121 h	950 °C	ESC
	8.7 ppm	142 h	950 °C	ESC
	30 ppm	varied	800 °C	ASC
	60 ppm	varied	800 °C	ASC
	150 ppm	varied	800 °C	ASC
Tar				
Toluene	25 ppm	500 h	800 °C	ASC
	50 ppm	482 h	800 °C	ASC
	100 ppm	785 h	800 °C	ASC
	550 ppm	100 h	950 °C	ESC

Contaminant concentrations in the fuel gas

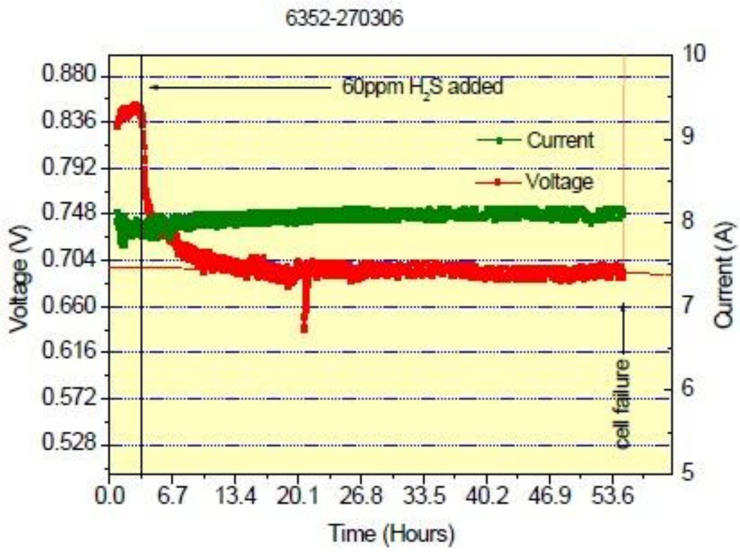
The measurements were performed on both electrolyte supported (ESC) and anode supported cells (ASC). All cells had an electrochemical active are of 16 cm^2. Both types of cells feature a nickel/8YSZ anode though of different composition and micro structure. The cells are measured in all alumina housing with platinum cathode contacts and nickel anode contacts. The cell is sealed using gold gaskets. The concentration of the contaminants but for toluene and hydrogen chloride were controlled by adding mixtures of the contaminant in nitrogen to the main fuel feed. Toluene and hydrogen chloride were added by saturating an additional nitrogen flow. The saturation was accomplished by controlling the gas temperature after passing the nitrogen through the liquid toluene or saturated hydrogen chloride solution in water. The experiments with the ESC were performed at 950° C and a current density of 150 mA/cm². The experiments with the ASC were performed at 800° C and at a current density of 500 mA/cm².

For most of the contaminants tested there was no measurable influence on the performance of the cells. The results for hydrogen chloride are to be considered with some caution because of difficulties with the test rig. During the course of the experiment no effect could be observed. The only contaminant with a noticeable effect was hydrogen sulphide both for ESC and ASC. For low concentrations of 1 ppm in the experiments using ESC there is no noticeable effect in the short term experiments. At higher concentrations a drop in the cell voltage can be observed shortly after the adding of the contaminant. At 4 ppm this effect seemed to be reversible. At 8.7 ppm the cell voltage increases after the removal of the contaminant but does not reach the voltage from before the measurement. Measurements on ASC at 800° C under higher H2S concentrations show a similar drop in cell voltage after addition of the contaminant to the fuel feed. During operation the cells failed without any noticeable warning. Also the time till failure could not be correlated to the amount of H2S in the fuel feed.

The data obtained in our laboratory indicate that the electrochemistry of the anode of the SOFC is insensitive to most fuel contaminants. The only real problem is posed by sulphur containing compounds. At higher concentrations the anode is irreversible damaged. Unfortunately, there is no correlation between the concentration of the H2S and the life time of the cell. There is also no indication in the data announcing the failure of the cell.



Influence of the H2S concentration on the cell performance of an ESC at 950° C



Influence of the H2S concentration on the cell performance of an ASC at 800° C

These experience carried out from the partner Juliech highlighted how the topic of SOFC poisoning with a strong impact on:

- *Technology lifetime*: in the mean that fuel feed and pollutant may effect SOFC efficiency not only in the short time but during operation;
- *SOFC cost*: in the mean that the experimental feasibility of coupling fuel cell with innovative fuel (such as biofuels) may permits design of plant with higher economical feasibility.

In addition comparing listed results with literature came out that for most pollutant no low temperature test was performed, all experience were performed with pure hydrogen and no real gasmix was used and lower type of pollutant were tested with not unique results. In addition several tests, such on HCl ones, were performed in non-optimal conditions and require to be repeated, compared and improved. Finally long term effect of pollutant was not investigated. To enhance and improve experience on gas pollutant of SOFC and offering a unique facility for this specific test following upgrade are needed:

- Improvement of fuel feed variability in terms of gas flows, gas mix and type of pollutant;
- Improvement of online analysis instrumentation and methods to support any modelling activity and to evaluate degradation analysis in long term tests;
- Improvement of post analysis techniques;

A join research permitted to share common activities and methods and to develop an infrastructure of the three laboratory offering high quality and coherent methodology and instruments. These activities permits an easier compare of results between different laboratories in the same topic with the possibility to develop a round robin internally in the project or in TNA from an external body that may be interested in comparing different results or realize a common access.

Description of improvements achieved within the H2FC EU Infra project

From the indication emerged during the history analysis the SOFC fuel cell test rig was improved to investigate the effect of contaminants such as H_2S, SO_2, TAR. To perform test with gas streams containing these compounds a redesign of a test rig was performed. This is required by the risk of adsorption of the components that causes a reduction of the contaminant quantity into the cell. Standard steel lines have to be substituted with special pipes in sulfinert and all instrumentations, such as flow meters, thermocouples and pressure sensors has to be realized to be resistant to sulphur and, at the same time, to reduce adsorption. The aim is to obtain a test facility able to realize different type of test, measuring the cell performance in terms of main cell characteristics: voltage, current and temperature. In addition the test rig has to guarantee the correct operation of the cell as described in the start-up procedure. This usually requires a specific ramp rate to reach operative temperature, a “safety” flow mix, mainly nitrogen based, and a mechanical load on the cell to guarantee the continuous contact between the cell and the system. With the aim of having all functions required, the rig approach is divided in 6 subsystems: cell housing, thermal management, temperature and voltage measurement, gas control, mechanical load and current control.

The aim of system upgrade is to increase potentiality of pollutant test to evaluate effect on cell degradation. A particular focus was given to H2S and H2S contaminants and TAAR. This decision required a particular focus on gas supply system where is required to avoid gas mix containing pollutants flowing inside the bubbler that is usually used to humidify the gas stream. The suphur is soluble in water and if the flux containing pure H_2S or other compounds goes inside the water tank no contaminant will reach the cell. Thus a bypass was added to the pipelines to allow polluted gas to be mixed with the clean stream after humidification. Finally the detection of sulphur in the gas requires special electrochemical sensors. These sensors permit a preliminary evaluation if sulphur content is above 2 ppm (e.g. biogas) but when the concentration is below this value or other contaminants are present a gas chromatography technique is required. The UP implemented a method using a GC Dani with FPD detector and Restech Rxi-1m2 column to measure quantities that can reach down to 10 ppb. Thanks to several calibration standards available in laboratory the GC can also identify what kind of sulphur compound is present in the flue gas and permits, if required, to give inputs to reproduce any gasmix that may be required by any private company interesting in testing SOFC fed by biogas or odorized natural gas.

GC system for pollutant measure (GC DANI) and for online gas analysis (C2V)

In additional a fast GC analyzer (C2V) was used to implement a technique to measure total flow and quality of anode off gases. The method permits to measure main gas composition that can be used to evaluate the effect of contaminants in internal reaction especially for composition such as syngas and biogas.

When solid fuel is gasified the process produces three different compounds: char, TAR and syngas. While solid char is a waste product TAR can be separated as well or valorized inside the system. To evaluate the effect of TAR in high temperature fuel cell a system was developed to flow small quantities of liquid TAR (such as toluene) into a gas stream simulating syngas composition. A very simple system was developed by flow the gas stream into liquid toluene kept at controlled temperature. The flow is mixed with a clean flow and the target composition of toluene into the stream is obtained. Following the request of a potential user a preliminary validation of the system was performed comparing expected mass reduction of toluene with measured one. The stream was also sent to an operating SOFC and the expected increase of performance was obtained. The new methodology permits to perform evaluation of TAR effect with a wide range of syngas composition and TAR typology.

Big effort was dedicated also to post analysis evaluations. In particular following techniques typical of material analysis were evaluated: SEM, XRD, EDS, TEM, XRF. Particular focus was given to SEM and EDS that are is the most suitable analysis taking advantage of high quality existing infrastructure at University of Perugia that was never used for SOFC application. A specific method was development to analyze SOFC material with specific focus to anode reoxidation and carbon deposition.

Gemini Zeiss SEM microscope

Finally a system for EIS analysis was integrated into the test rig. The system is based on coupling a wave generator (Agilent 33120A) and an electrical load (Agilent N330x). A software in Labview was developed to perform the analysis and build the main plots (Nyquist, Bode). The developed system permits to cover spectrum from 0.1 to 10000 hertz.

System developed to perform toluene pollution and EIS set-up

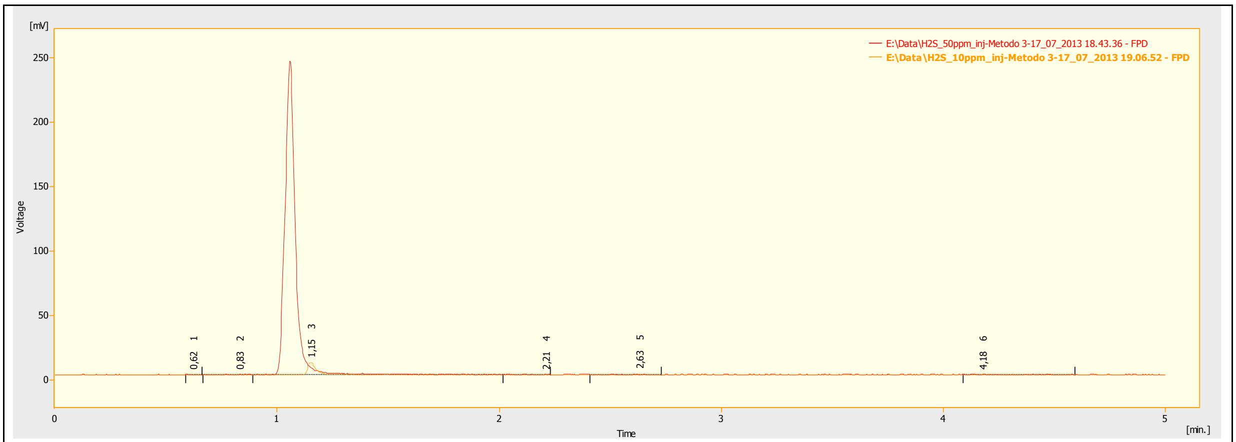
First results showing that improvement was successful

Main results obtained where in the field of gas chromatography implementation, SEM analysis and EIS. This paragraph contains main results obtained showing that improvements were successful.

An important result achieved was the implemented gas chromatography method to analyse H_2S and H_2S compounds. In this specific case typical natural gas compounds where chosen: TBM, usually added as odorant, and DMS, that is present originally in the gas and can still be present at final user.

GC Calibration H2S:

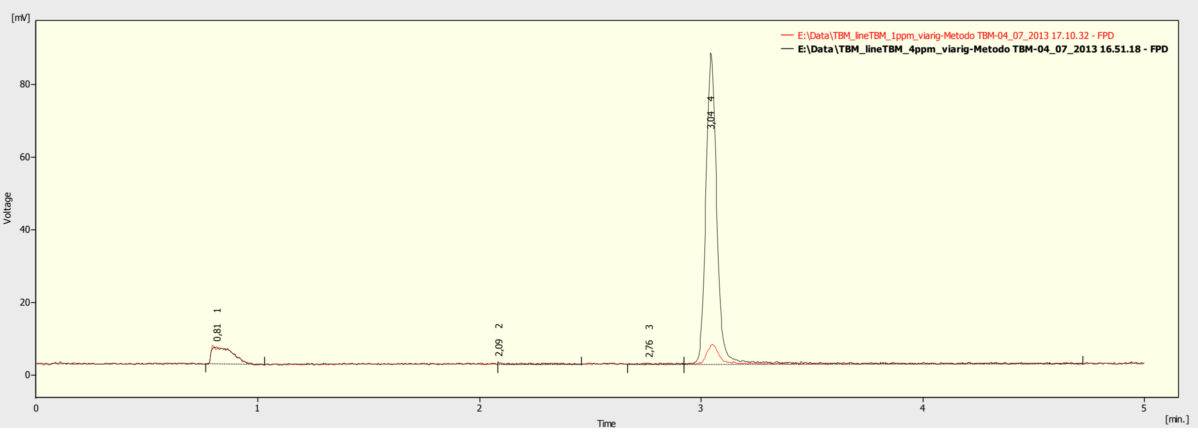
The test shows the sensitivity of GC down to 10 ppm of H2S and gives data for the calibration curve (in this case linear). The gas used is the standard certified H2S in N_2 – 200 ppm diluted in the test rig down to required concentration. The results show the feasibility of the instrumentation and of the method. Minimal improvement are required to go to lower values of H_2S ppm.



Calibration GC H2S		Linearization	
ppm H2S	Peak Area [mV s]		
10	49.48	m	18.81
50	800.89	q	-139.61

GC Calibration TBM:

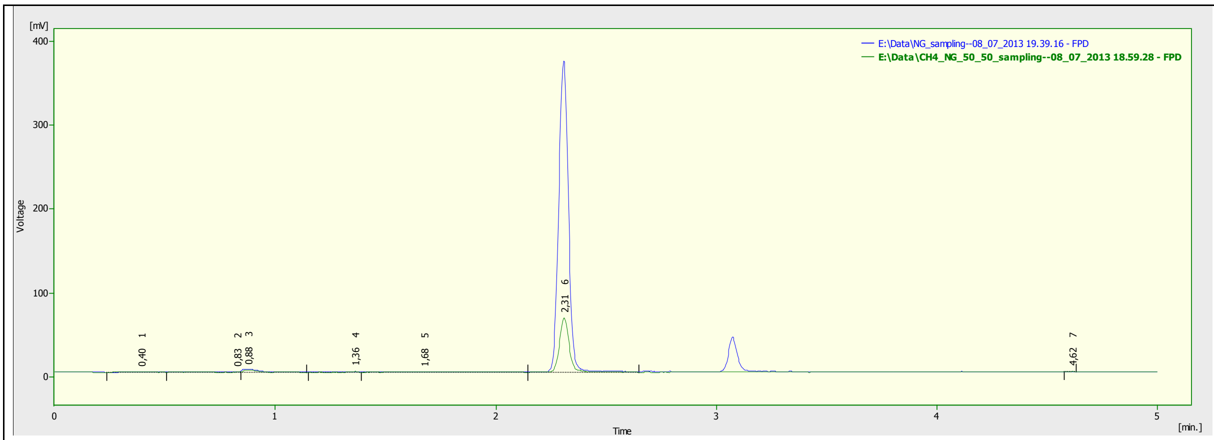
The test shows the sensitivity of GC down to 1 ppm and gives data for the calibration curve (in this case linear). The gas used is the standard certified TBM in CH_4 – 50 ppm diluted in the test rig down to required concentration.



Calibration GC TBM (online)			Linearization	
ppm TBM	mg/m^3 TBM	Peak Area [mV s]		
1	3.68	29,37	m	0,0102
4	14.72	324,88	q	0,7018

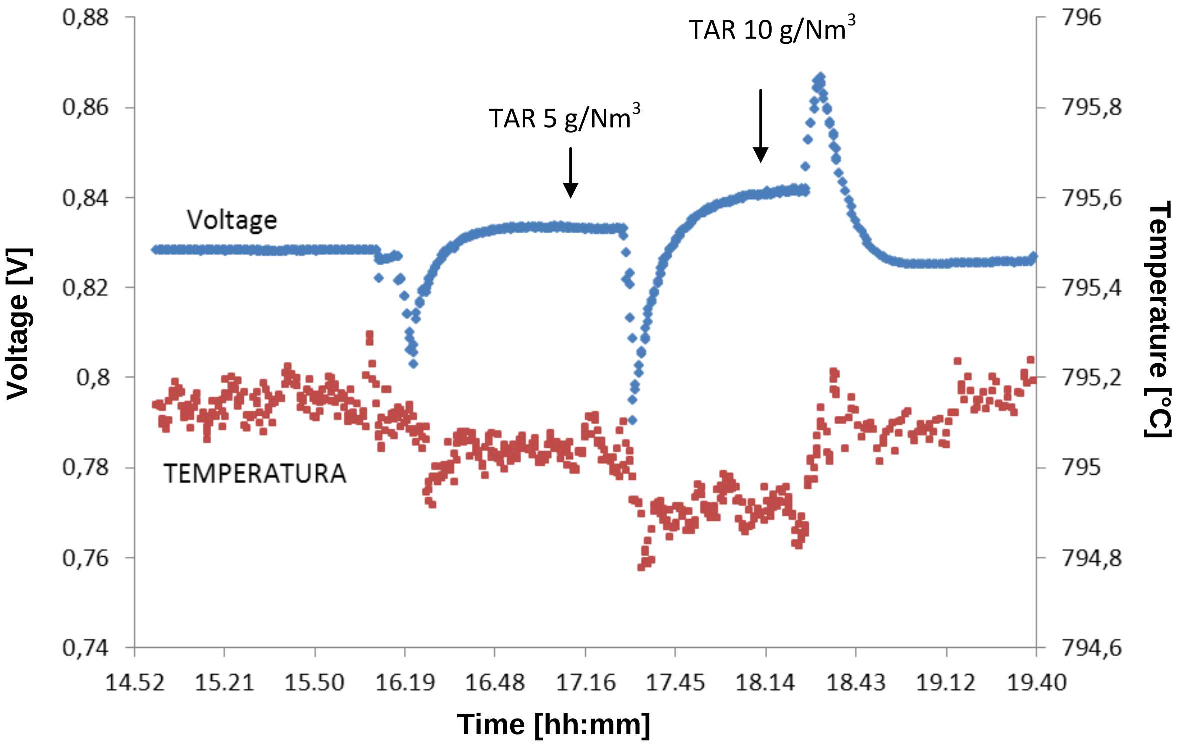
GC Calibration DMS:

The test shows the sensitivity of GC down to 3.39 ppm of DMS and gives data for the calibration curve (in this case linear). The gas used is natural gas that was certified by an official national laboratory.



Calibration GC DMS (syringe)			Linearization	
ppm DMS	mg/m^3 DMS	Peak Area [mV s]		
6.77	17.2*	1080.35	m	0.0038
3.39	8.6	179.42	q	2.7109

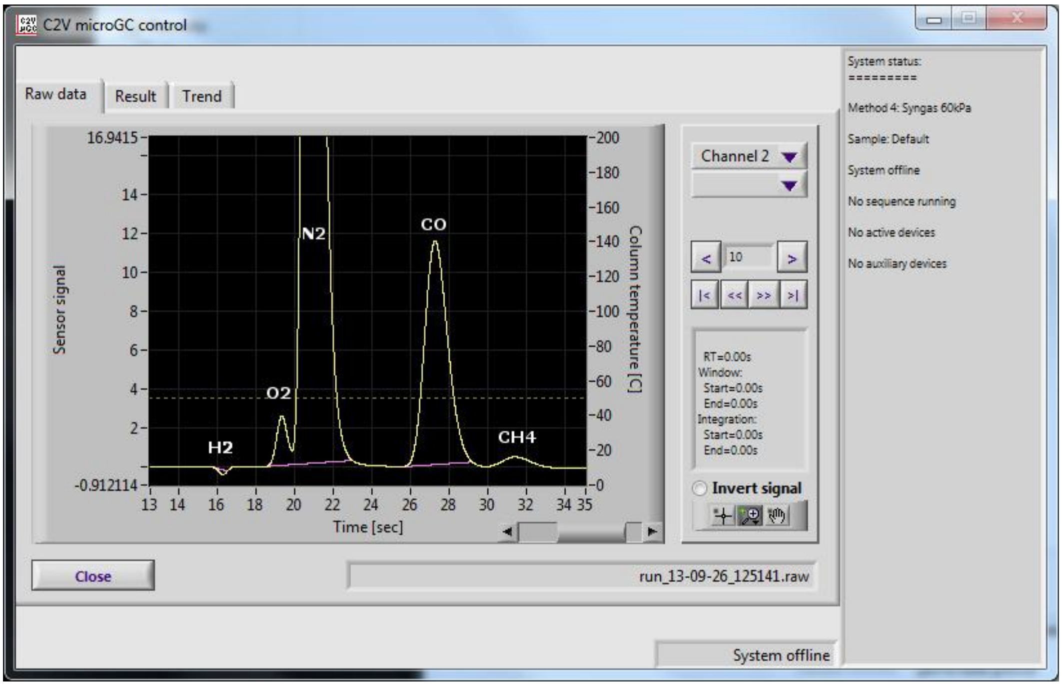
The study of the effect of pollutant into the cell is realized with simulated gas stream and model TAR. The test rig upgrade permitted to perform a wide range of gasmix and to introduce a specific quantity of TAR. Following image shows results obtained with a simulated syngas and increasing quantity of TAR.



H_2 [Nl/h]	N_2 [Nl/h]	CO_2 [Nl/h]	CO [Nl/h]	CH_4 [Nl/h]
1.7	10.6	3.4	2.1	0.45

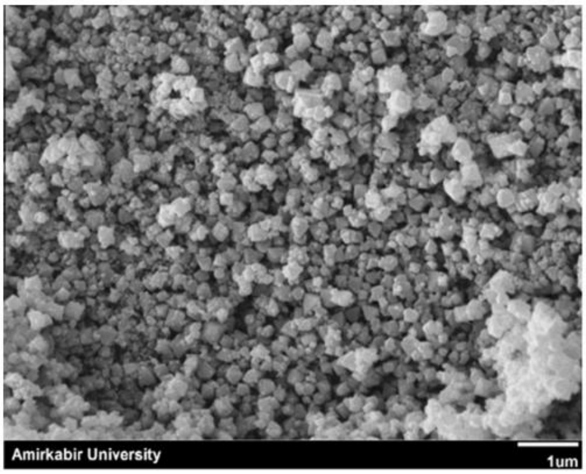
TAR diluted in syngas: effect on single cell voltage

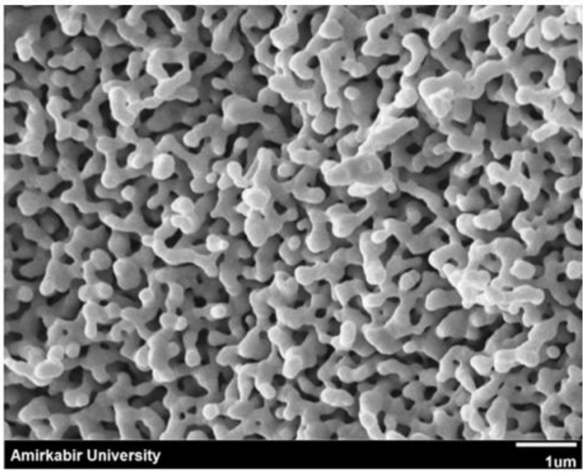
Gas chromatography techniques were improved also on a second gas chromatograph, C2V, that permits off gasses analysis. This instrumentation is useful to evaluate internal reaction and to verify fuel cell operative condition. Here below is shown a chromatogram typical of syngas containing CO, CO2, N2 and CH4. This type of composition is the gas stream used in simulated application where a model TAR is diluted.

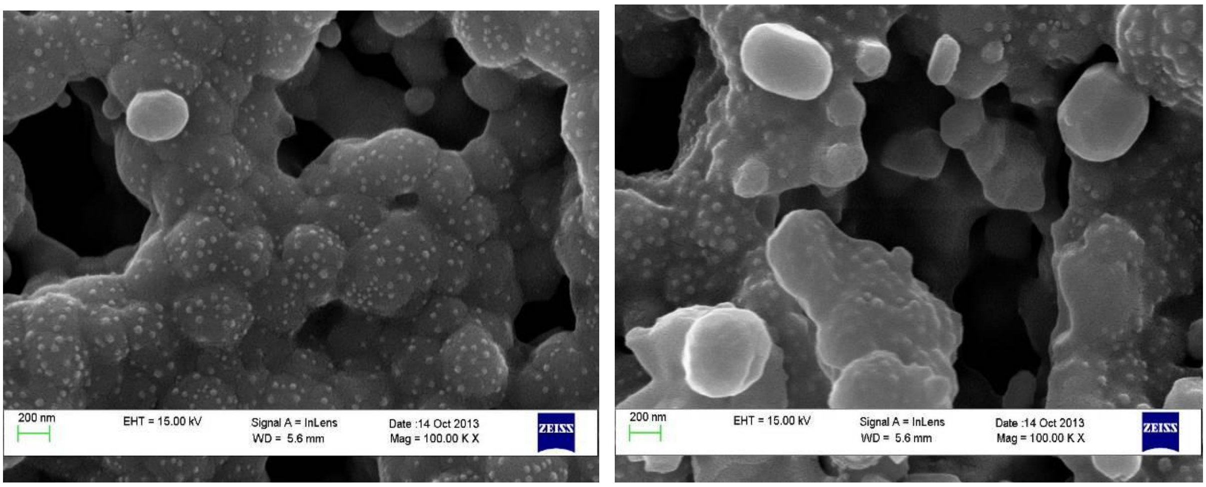


Chromatogram of SOFC off gasses when fed with syngas

A very potential improvement was obtained thank to the implementation of SEM method for SOFC analysis. Here below are reported some results obtained during the activities that show as high quality results were obtaining reaching image with zoom down to 100 KX. The method permitted to study cell morphology such as reduction or oxidation and carbon deposition.

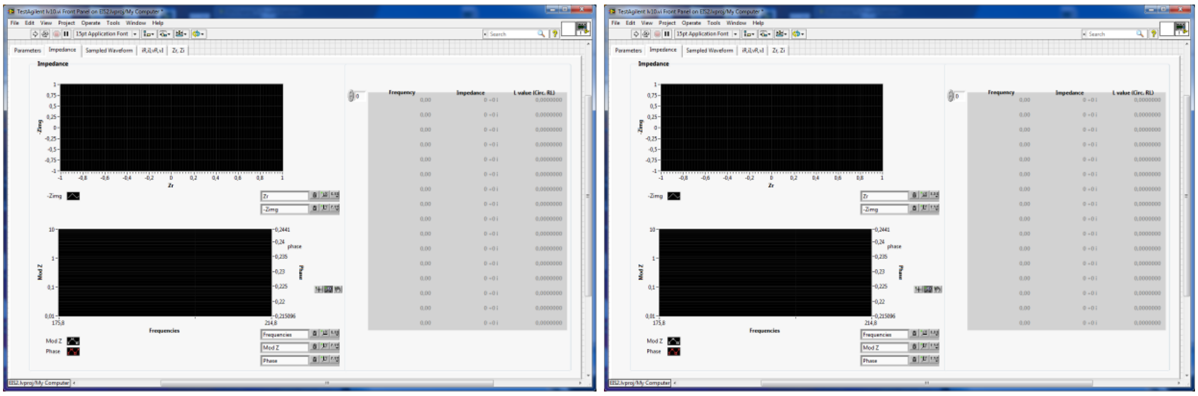




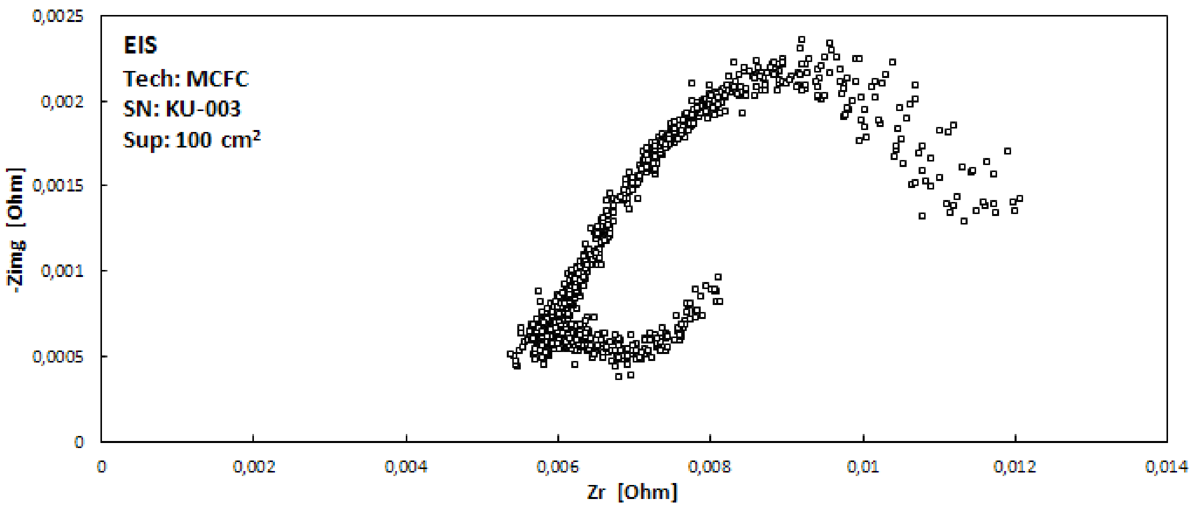


SEM images obtained with the developped method

Finally the EIS spectroscopy technique was implemented. In this case existing instrumentation was integrated and a specific software was improved to perform the analysis. Preliminary results in MCFC showed how the analysis was successful and the method is validated and ready to be used in both MCFC and SOFC facilities.



EIS control software



EIS analysis of a MCFC

Conclusion

The joint effort of all the partners permitted to give a significant upgrade to the facilities offered for TNA. The peculiar effort on effect of contaminants permitted to involved partners to offer highest experimental infrastructure compared to current state of the art. As example the literature available on TAR effect on SOFC shows that infrastructures used are equivalent or lower in terms of techniques and analysis compared to H2FC partners.

An important additional result came from the share of knowledge that permitted a quick improvement of techniques and methods enhancing the big effort of this and other European project in harmonizing test procedures and methods. This effort will be an additional value to be offered in TNA because results will be easier to be compared with other laboratories results and, more important, are likely to be equivalent with future European standards.

Deliverable was completed 100%.