Degradation Signatures identification for stack operation diagnostic

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1. TEST PLAN

Accordingly to the decisions taken after the GENIUS-DESIGN Workshop held in Brussels on February the 17th, 2011, the experimental activity will focus on the investigation of three degradation mechanisms:

1. Anode oxidation due to high local fuel utilisation (that will be simply called "High Fuel Utilisation");
2. Carbon deposition ("C deposition");
3. Leakage of air into the anode side ("Leakage")

This deliverable is meant to define a test plan to simulate the faults associated with the first two mechanisms only. The test plan concerning the third mechanism is postponed to allow further discussion on how to simulate such a fault from a technical stand point.

It is important to notice that one Single Cell (SC) and/or one Single Repeating Unit (SRU) should be dedicated to simulate only one fault. On the other hand, the same fault should be conducted on several SCs and SRUs.

High Fuel Utilisation

The fuel utilisation (*FU*) is related to the electrical current density (*i*), fuel composition and gas flow rates (Q_i) through the following equation:

$$FU = \frac{\dfrac{i \cdot A_{fc} \cdot n_{cell}}{2F} \cdot 22.4136 \cdot 6 \cdot 10^4}{\left(Q_{H_2} + Q_{CO} + 4Q_{CH_4} + 7Q_{C_2H_6} + 10Q_{C_3H_8} + 13Q_{C_4H_{16}} \right)}^1 \tag{1}$$

where n_{cell} is the number of stack cells, F is the Faraday constant[2] and A_{fc} is the cell active area.

The high FU fault is simulated by either increasing the current density or decreasing the total gas flow rate with respect to the nominal values defined in Table 1, while all the other control variables are kept at their nominal value.

Control Variable	Nominal value				
Current density (A/cm^2)	0.30 (ESC)/ 0.50 (ASC)				
Total inlet gas flow rate (ml/(cm^2 s))	5.62 (ESC)/ 9.37 (ASC) (FU = 0.60)				
Fuel composition (volumetric %)	CH$_4$	H$_2$O	H$_2$	CO$_2$	N$_2$
	14.02	28.04	5.90	1.85	50.18
Air Utilisation (%)	20				
Furnace temperature (°C)	750				

Table 1 – Nominal operating conditions

Therefore, the current density has to be increased stepwise from the value corresponding to a *FU = 0.60* up to *FU = 0.90*. Each step in current density should be gradual (with a ramp of 0.10 A (cm^2 min)$^{-1}$) and correspond to a step in *FU* of *0.10*. Once the step value is reached, the operating condition should be kept for

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[1] This equation holds for gas flow rates measured in Normal Conditions (i.e. 1 bar and 0°C)
[2] F= 4 96485.3383 A*s/mol (CODAT2005)

20 to 24 hours. After such a period of time, the current density should be brought back to its nominal value and kept for 20 to 24 hours before a new step is made.

Consequently, the experimental points to perform are presented in Table 2 and 3 for Electrolyte Supported Cells (ESC) and Anode Supported Cells (ASC) respectively.

Experiment Number	Current Density (A/cm^2)	Residence time (h)
0	0.30 (FU=0.60)	20-24
1	0.35 (FU = 0.70)	20-24
2	0.40 (FU = 0.80)	20-24
3	0.45 (FU = 0.90)	20-24

Table 2 – High FU fault simulation with current density: experimental points for ESC

Experiment Number	Current Density (A/cm^2)	Residence time (h)
0	0.50 (FU=0.60)	20-24
1	0.58 (FU = 0.70)	20-24
2	0.67 (FU = 0.80)	20-24
3	0.75 (FU = 0.90)	20-24

Table 3 – High FU fault simulation with current density: experimental points for ASC

The test plan is to start running the SC or SRU on pure hydrogen and wait long enough for the performance to stabilise. This is expected to take on the order of 100 hours. The conditions for this stabilisation period are: ASC 0.5 A/cm^2 & 9.37 ml/ cm^2/min (pure H$_2$), ESC 0.3 A/cm^2 & 5.62 ml/ cm^2/min (pure H$_2$). However, if performance stabilisation is not reached after 96 hours, the tester may decide to stop the experiment. On the other hand, once the performance is stable, the SC or SRU should be brought to the nominal operating conditions (Table 1), which also means *experiment 0* in Table 2 and 3. Thereafter, the test plan is carried on by going from *experiment 0* to *experiment 1* ramping the current with a rate of 0.10 A (cm^2 min)$^{-1}$, remaining at this condition for 20-24 hours, ramping the current down to *experiment 0* again, allowing a 20-24 hour residence time, and then going to *experiment 2*, etc. For each experimental condition given in Table 2 and 3, EIS spectra, polarization curves, gas chromatography etc. should be carried out.

As mentioned above, the high FU fault is also simulated by decreasing the total inlet gas flow rate. This should be done following exactly the same approach explained for the current density. The experimental conditions are listed in Table 4 and 5.

Experiment Number	Total Inlet Gas Flow Rate (ml/(cm^2 min))	Residence time (h)
0	5.62 (FU = 0.60)	20-24
1	4.82 (FU = 0.70)	20-24
2	4.22 (FU = 0.80)	20-24
3	3.75 (FU = 0.90)	20-24

Table 4 – High FU fault simulation with inlet gas flow rate: experimental points for ESC

Experiment Number	Total Inlet Gas Flow Rate (ml/(cm^2 min))	Residence time (h)
0	9.37 (FU = 0.60)	20-24
1	8.03 (FU = 0.70)	20-24
2	7.03 (FU = 0.80)	20-24
3	6.24 (FU = 0.90)	20-24

Table 5 – High FU fault simulation with inlet gas flow rate: experimental points for ASC

Carbon deposition

This fault is simulated by changing the steam-to-carbon ratio (*S/C*) of the inlet fuel[3] as shown in Table 6, or, in alternative, the current density as shown in Table 7 and 8. The values have been chosen in order to pass the carbon deposition threshold (see Annex A) and be sure to have a carbon precipitation signal to look for.

Experiment Number	S/C	Residence time (h)
0	2	20-24
1	0.2	up to 96
2	0.0	up to 96

Table 6 – C deposition fault simulation with steam-to-carbon ration: experimental points

As in the previous case, the SC or SRU should be first stabilised with pure hydrogen feeding and then switched to the nominal operating conditions defined in Table 1 (which also correspond to *experiment 0* in Table 6) and let it run in that condition for about a day. Successively, the steam-to-carbon ratio should be decreased by a factor of 10 (*experiment 1*) and allow a residence time of up to 96 hours (performance stabilisation could be achieved in a shorter time, in such a case the residence time can be reduced to 24, 48 or 72 hours and it is possible to proceed to the next step). The SC or SRU should then be brought back to *experiment 0* in Table 6 and allow 20-24 hours of residence time. The same procedure should be followed to reach also *experiment 2* in Table 6.

The carbon deposition fault is also simulated by keeping the *S/C* ratio constant (i.e. 0.2) and decreasing the current density as illustrated in Table 6 and 7 for ESC and ASC, respectively. The stabilisation with hydrogen and the condition corresponding to *experiment 0* should be performed in the same way as described above. Thereafter, the *S/C* ratio should be decreased by a factor of 10 to reach *experiment 1*. Such condition should be maintained for a time of up to 96 hours. The tested device should be brought to *experiment 0* and *experiment 1* again and allow the relative residence time. Successively, from *experiment 1* the current should be ramped down with a rate of 0.10 A (cm^2 min)$^{-1}$ to reach *experiment 2* in Table 7 and 8 and wait for a time of up to 96 hours. The same procedure should be followed to reach also *experiment 3* in Table 7 and 8, that is the operating conditions should be brought back to *experiment 0* and *experiment 1* before going to *experiment 3*.

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[3]This means that the fuel composition is changed (steam fraction is decreased and nitrogen fraction is increased to maintain the same total inlet gas flow rate) while the other variables are kept at their nominal values (Table 1)

Experiment Number	S/C	Current Density (A/cm^2)	FU	Total Inlet Gas Flow Rate (ml/(cm^2 min))	Residence time (h)
0	2	0.3	0.6	5.62	20-24
1	0.2	0.3	0.6	5.62	up to 96
2	0.2	0.2	0.4	5.62	up to 96
3	0.2	0.1	0.2	5.62	up to 96

Table 7 – C deposition fault simulation with current density for ESC: experimental points

Experiment Number	S/C	Current Density (A/cm^2)	FU	Total Inlet Gas Flow Rate (ml/(cm^2 min))	Residence time (h)
0	2	0.5	0.6	9.37	20-24
1	0.2	0.5	0.6	9.37	up to 96
2	0.2	0.4	0.48	9.37	up to 96
3	0.2	0.3	0.36	9.37	up to 96

Table 8 – C deposition fault simulation with current density for ASC: experimental points

2. VARIABLES TO MEASURE

During the entire duration of the experiments, the variables listed in Table 9 should be recorded with the highest possible sampling rate (1 Hz).

	Variable Description	Symbol	Sampling rate (Hz)
Control Variables	Current Density	i	1
	Total inlet gas flow rate	Q_{IN}^{gas}	1
	Fuel composition	x_{OUT}^{gas}	
	Furnace temperature	T_{furn}	1
Monitoring Variables	Single Cell/Stack Voltage	U_{cell}/U_{stack}	1
	Inlet Temperature (fuel, air)	T_{IN}^{f}/T_{IN}^{a}	1
	Outlet Temperature (fuel, air)	T_{OUT}^{f}/T_{OUT}^{a}	1
	Cell/Stack[4] Temperature	T_{cell}/T_{stack}	1
	Outlet Gases Flow Rates	Q_{OUT}^{gas}	
	Inlet Anode/Cathode Pressure	p_{IN}^{an}/p_{IN}^{ca}	1
	Outlet Gas Composition	x_{OUT}^{gas}	
	Air Inlet/Outlet Relative Humidity	$\varphi_{IN}^{air}/\varphi_{OUT}^{air}$	
	Anode Outlet Oxygen Content	$x_{OUT}^{O_2}$	

Table 9 – Variables to measure

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[4] Measured on the solid of the cell / SRU housing, in the middle, for stacks it could be either the mean of inlet and outlet gas temperature or the temperature of the metal in the middle of the stack.

3. RAW DATA FORMAT

As mentioned in the previous section, all the measured variables should be stored with 1Hz sampling rate. However, it is clear that this is not feasible for some of them, such as the outlet gas composition or the electrochemical impedance spectroscopy data. Subsequently, it is recommended that only variables with the same sampling rate are saved together in a single text file, which means that there should be one file per each sampling frequency.

Therefore, the following step should be followed for raw data formatting:

1. **Arrange the files in the hierarchical structure illustrated in Fig.1**.

   Starting from the faults simulation defined in Table 2 through 6, create:
   - ♦ a folder for each fault;
      - ➢ a subfolder for each control variable (if more than one) used to simulate the fault;
         - ▪ a subfolder for each Single Cell (SC1, SC2, etc.) and Single Repeating Unit (SRU1, SRU2, etc.);
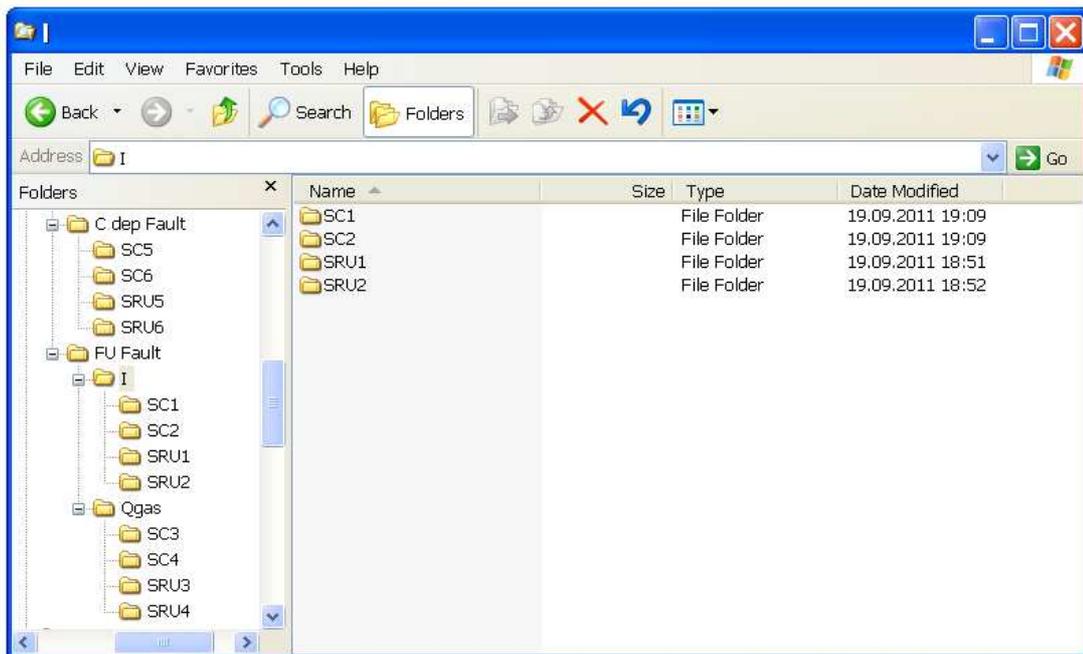

Figure 1 – Example of directories hierarchical structure

2. **Generate a single data file for each sampling rate**

3. **Name the file with the following string**:

   YYMMDD_hhmm_hierarch

   a. where *YYMMDD* corresponds to 2 digits for year, month and day;

   b. *hhmm* corresponds to 2 digits for hour and minute;

c. *hierarch* corresponds to the type of file in the hierarchical structure (*MAIN*, *EIS*, *IV* or *others*) as clarified in the next point

4. **save the files in the corresponding folder (see Fig. 2 for example)**

The file with the suffix *MAIN* contains all the data including polarization curves and the transient phases, whereas the recorded EIS spectra and polarization curves will be contained in separate files (i.e. 110915_1409_EIS.txt, 110915_1521_IV.txt. etc.)
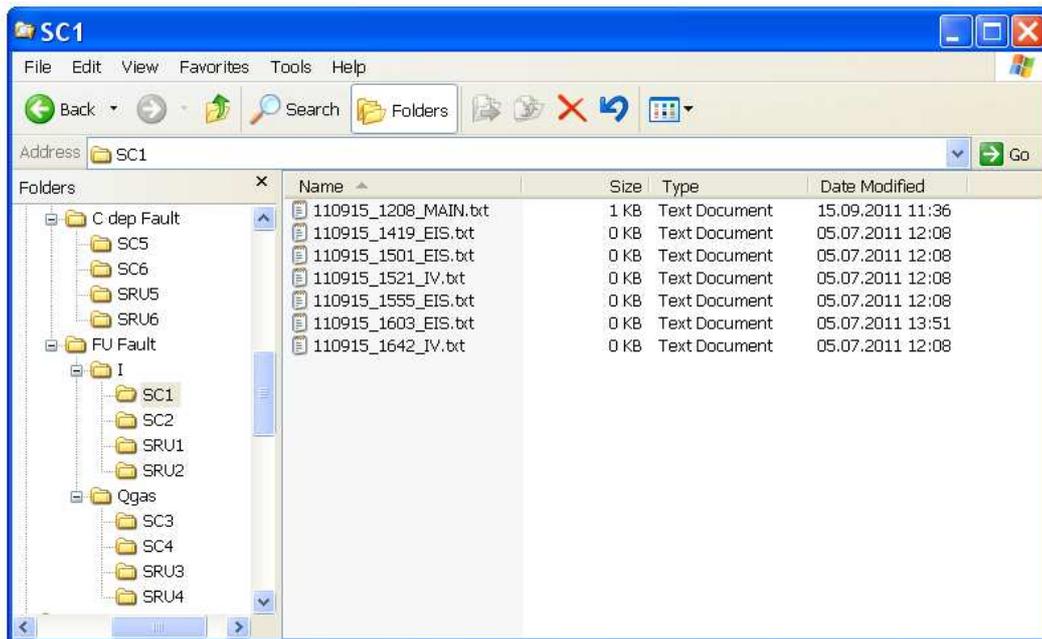

Figure 2 – Example of hierarchical structure of raw data files

5. **in the MAIN file, arrange the data in columns with the following order (see Fig. 3 for example)**

"time [s]" "expn" "state" "voltage [V]" "current density [A/cm^2]"…

a. "expn" corresponds to the experiment number provided in Table 2 through 7

b. "state" corresponds to the type of operation the system is running at. It can take only 3 values:

(i) state = 2 when an I-V curve is carried out

(ii) state = 1 when a EIS spectra is carried out

(iii) state = 0 at all time when it is neither 1 nor 2

Figure 3 – Example of "MAIN" data file

Annex A: Determination of carbon deposition conditions

In order to cause carbon deposition it is possible either to decrease the Steam-to-Carbon ratio by replacing steam with nitrogen in the inlet fuel mixture maintaining all other parameters constant or decreasing the current density. Owing to the pseudo equilibrium diagram provided below with the chosen fuel corresponding to an S/C ratio equal to 2, no carbon precipitation is expected even at OCV.

For that reason, to have carbon deposition and hence a signal to look for, alternative operating conditions are proposed consisting either by decreasing S/C ratio at nominal current value (0.5 A/cm^2 for ASC, 0.3 A/cm^2 for ESC) or by decreasing current density keeping the S/C ratio at a lower value (0.2) than the nominal one (2) in order to cross the carbon precipitation threshold shown in Fig. A1 (for ASC).
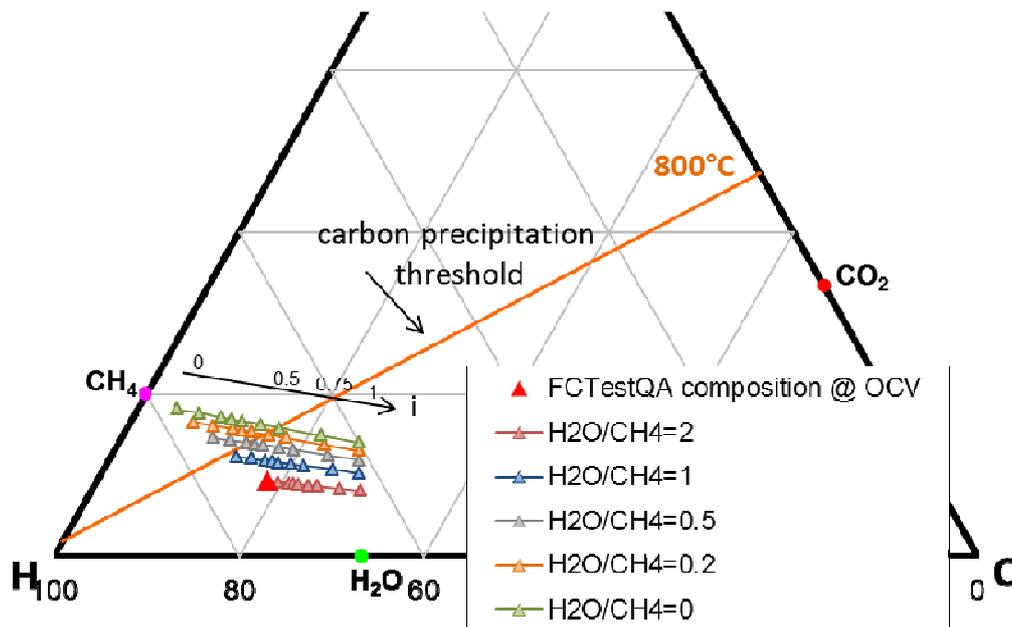

Figure A1 – Ternary diagram H-C-O to investigate the inlet fuel composition and current density with respect to carbon precipitation threshold for ASC.