Project Deliverable

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PU	Public	**PU**
PP	Restricted to other program participants (including the Commission	
RE	Restricted to a group defined by the consortium (including the Commission)	
CO	Confidential, only for members of the consortium (including the Commission)	Public

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Abstract :

The aim of this deliverable is to act the tests protocols used during the Sapphire project. It is an update of the deliverable 2.3 and describes all the tests that have been performed during the project from single cell to system levels.

Keywords :

PHM, Profile, Characterisation, Measurement

Revision History

Rev.	Date	Description	Author (Organisation)
1	13/03/2016	1st draft	Philippe MOÇOTÉGUY (EIFER)
2	06/04/2016	2nd draft	Philippe MOÇOTÉGUY (EIFER)
3	02/05/2016	Final version	Philippe MOÇOTÉGUY (EIFER)

Table of Content

1 Tests under CO poisoning

A 20 cell stack was equipped with various membrane electrode assemblies to investigate the different behaviour to catalyst contamination. Operating conditions were derived from the µCHP-system and are summarized in Table 1.
After some waiting hours at low stationary voltage level, increasing and decreasing steps in air bleed were performed to see the performance change. The cells that are the most similar to the µCHP-system were used to implement an air bleed controller which was validated with a 13 cells stack.

Operating parameter	Value
Current density	0.125, 0.228, 0.35 A/cm²
Stack temperature	60°C
Relative gas inlet humidity	91%
Anode gas inlet composition	75% H_2, 25% N_2. Contamination by: 4, 8 and 16 ppm CO. Steps in air bleed: 0-1.6%
Cathode gas inlet composition	100% air
Anode gas stoichiometry	1.5
Cathode gas stoichiometry	3.0
Gas outlet pressure	Ambient

Table 1: Operating conditions of CO tests.

2 Accelerated stress tests

2.1 Single cells

2.1.1 Evaluation of membrane chemical stability

The tests aiming at evaluating the chemical stability of the membrane were adapted from the DOE AST protocols.
The cells were hold at OCV, at a temperature of 90% under hydrogen and air flow rates. Both compartments were pressurized at 1.5 bars. The inlet relative humidities of hydrogen and air were fixed at 30% (i.e. dew point temperature of 61°C). Their flow rates were equivalent to an overstoichiometric ratio of 5 for a current density of 0.2 A/cm².
The fuel cell performance was evaluated after 24h, 48h and 60h of operation by: polarization curve (Cf. § 4.1), quick current sweep (Cf. §4.2), Electrochemical Impedance Spectroscopy (Cf. § 4.3), Cyclic and Linear Sweep Voltammetry (Cf. §4.4).

2.1.2 Studies on catalyst degradation

The second series of experiments aimed at evaluating the impact of potential cycling on Pt catalyst degradation. It also derived from protocols defined by the DoE.
The cycling profile is shown in Figure 1. It consisted of 10s of operation at 0.6V and 30s at 0.9V and the changes between operating points consisted in ramps of 50 mV/s and 100 mV/s in ascending and descending directions.
The cells were operated at 80°C and under 1.5 bars in both compartments. The reactants gases were fully humidified hydrogen (at the anode) and nitrogen (at the cathode).

The tests were carried out during 30000 cycles or until the electrochemical surface area decreases by 40% or activity loss reaches 60% or performance is reduced by 30 mV at 0.8 A/cm².

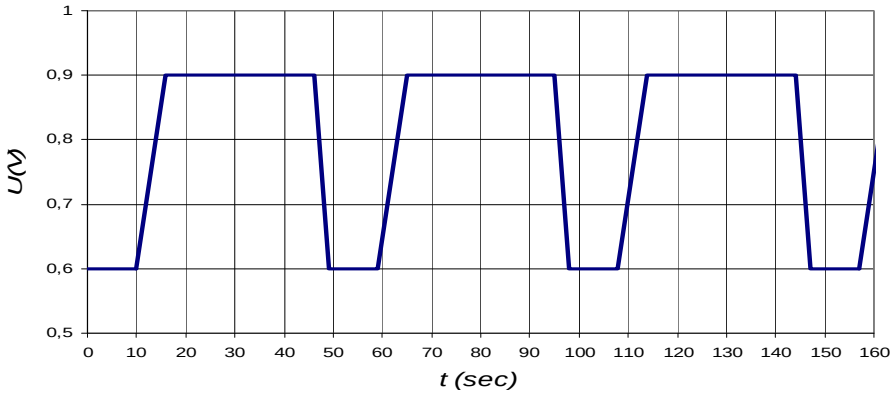

Figure 1 Cycle profile for potential cycling stress test at FESB experiments

The following diagnostic tests were performed at the beginning of life and after 1000, 3000 and 5000 cycles: polarization curve, quick current sweep, EIS and LSV. Cyclic voltammetries were also performed at the beginning of life and after 30, 100, 300, 1000, 3000 and 5000 cycles.

2.1.3 Degradation in simulated drive cycle

The experiment was conducted using slightly modified US06 drive cycle (Cf. Table 2) that was repeated for 1500 cycles:

		Current density (mA/cm^2)	
Step	duration (s)	Up to 850 cycles	After 850 cycles
1	15	0	0
2	20	200	200
3	20	400	400
4	12	20	0
5	18	200	200
6	18	400	400
7	15	20	0
8	20	200	200
9	20	400	400
10	12	20	0
11	20	200	200
12	30	Linear increase from 200 to 1000	Linear increase from 200 to 1000
13	20	1000	1000
14	30	800	800
15	10	20	0
16	20	400	400

Table 2: Characteristics of simulated drive cycle.

The cell was operated with air and pure hydrogen at a total pressure of 1.5 bars and overstoichiometric ratio of 2. After 1000 cycles, operating conditions were changed to accelerate the degradation process: Cell temperature was increased from 65°C to 70°C. This resulted in a decrease of relative humidities from 83% to 67% at the cathode and from 100% to 80% at the anode.
The following diagnostic tests were performed at the beginning of life and after 300, 600, 1000, 1200 and 1500 cycles: polarization curve. (Cf. § 4.1), quick current sweep (Cf. §4.2), Cyclic and Linear Sweep Voltammetries (Cf. §4.4).

2.2 Short stacks

The short stacks were cycled to quantify the catalyst degradation. The chosen accelerated stress test (AST) procedure is similar to the one selected for single cells (Cf. §2.1.2).
Despite the DOE AST protocol is defined in potentiostatic mode and in order to avoid some cells reversal during the test, the stack was cycled in galvanostatic mode between two constant current levels. The limits of current range were defined from the first polarization curves. The current density at which the best performing cell operates at 0.7V is chosen as the upper bound. The corresponding anodic and cathodic overstoichiometric ratios were respectively fixed at 1.3 and 2. The current density at which the best performing cell operates at 0.9V is chosen as the lower bound. The corresponding anodic and cathodic overstoichiometric ratios were: 1.5 and 3.
The stack was cycled under air and simulated reformate for a more precise adjustment of single cell voltages. The inlet gases were fully humidified.

3 Long term duration tests

3.1 Short stacks

The profile used for the long duration term tests is given on Figure 1 and the different phases are reported in Table 2.

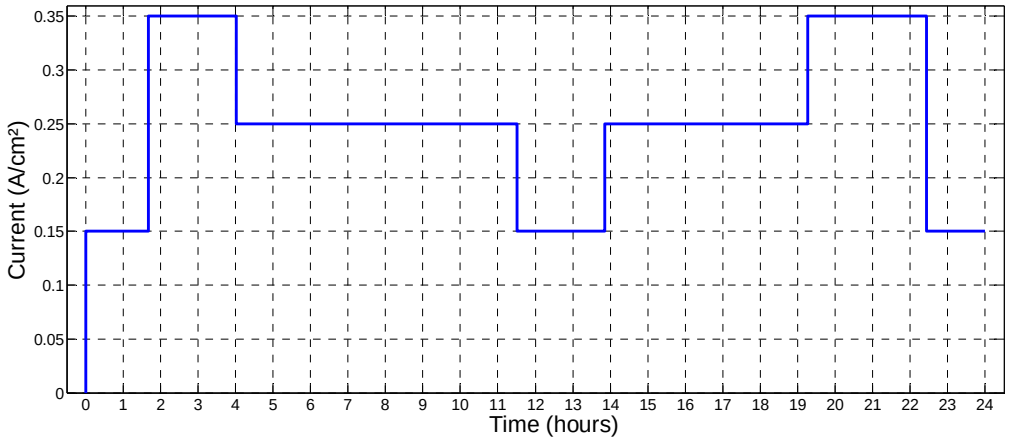

Figure 1 – Current profile applied to short stacks for long term testing

acc. time	hold time	hold time	current density	anode stoic.	cathode stoic.
sec	sec	min	A/cm²	λ_{fuel}	λ_{ox}
0	3	0,05	0,00	1,50	3,00
3			0,15	1,50	3,00
450	447	7,45	0,15	1,50	3,00
450			0,15	1,50	3,00
6060	5610	93,5	0,15	1,50	3,00
6060			0,35	1,30	2,00
14460	8400	140	0,35	1,30	2,00
14460			0,25	1,40	2,50
41460	27000	450	0,25	1,40	2,50
41460			0,15	1,50	3,00
49860	8400	140	0,15	1,50	3,00
49860			0,25	1,40	2,50
69360	19500	325	0,25	1,40	2,50
69360			0,35	1,30	2,00
80760	11400	190	0,35	1,30	2,00
80760			0,15	1,50	3,00
86400	5640	94	0,15	1,50	3,00

Table 3: Sequence of steps for endurance tests

The stacks were cycled during 2000 h under the conditions summarized in Table 4. One 5 cells stack was cycled with one cycle per day, while another stack was cycled with 10 cycles per day to evaluate the difference in performance degradation.

Operating parameter	value
anode gas stoichiometry	1.3 at 0.35 A/cm²
	1.4 at 0.25 A/cm²
	1.5 at 0.15 A/cm²
cathode gas stoichiometry	2.0 at 0.35 A/cm²
	2.5 at 0.25 A/cm²
	3.0 at 0.15 A/cm²
Average stack temperature	65°C
Relative gas inlet humidities on both compartments	100%
anode inlet gas composition	75% H2, 25% N2
cathode inlet gas composition	100% air
Gas inlet pressure at the anode	1.2 bars
Gas inlet pressure at the cathode	1.15 bars
Inlet gases temperature	60°C

Table 4: Operating conditions for duration tests on short stacks

3.2 Systems

Two Dantherm systems were tested. They were operated under air and reformed natural gas as follow:

1. 3000 hours of operation according to the load profile presented in Figure 2 and Table 5. Air bleed is controlled in the region 0.4-2.0% CO
2. 1000 hours of operation between 25A and 35A with weekly manual load change (Only performed on system 2 due to shutdown issues with system 1).
3. On-going operation according to the load profile presented in Figure 2 and Table 5 with the Sapphire controller implemented. Air bleed is controlled in the region 0.4-2.0%. CO test (Cf. § 1) is performed every 6 hours. One polarization curve is performed every week.

In all cases, the operating current is changed following a ramp of 20 $mA.cm^{-2}.min^{-1}$. This limitation is dictated by the thermal response of the reformer. The reactant stochiometries are controlled on the basis of Ballard recommendation for 1030 V3 cogeneration stack. Anodic overstoichiometric ratio is automatically regulated and governed by the system's thermal equilibrium. The cathodic overstoichiometric ratio is regulated according to operating current densities (Cf. Table 5).

I (A)	t_{step}(min)	T_{in} (°C)	T_{out} (°C)	$P_{a,\,in}$ (bar)	$P_{a,\,out}$ (bar)	$P_{c,\,in}$ (bar)	$P_{c,\,out}$ (bar)	s_c
15	140	50	57	1.105	1.045	1.047	1.004	2,3
35	140	57	67	1.18	1.095	1.106	1.013	2
25	410	57	67	1.125	1.066	1.074	1.007	2,05
15	140	50	57	1.105	1.045	1.047	1.004	2,3
25	330	57	67	1.125	1.066	1.074	1.007	2,05
35	200	57	67	1.18	1.095	1.106	1.013	2

Table 5 Profiles applied to the systems (including ramp time). (N.B.: At 15A, the temperature is marked in red because, even if setpoint is 57-67°C and due to system limitation, the cooling remains too high)

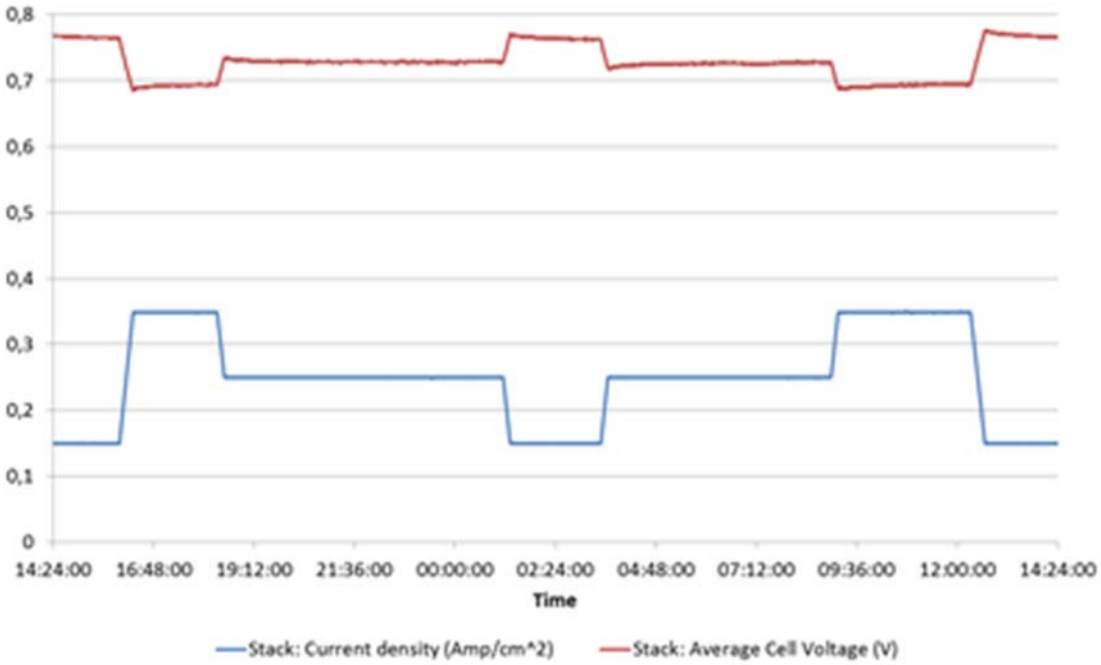

Figure 2: Dantherm's load profile

The following outputs are measured as part of the standard system.

- Stack coolant inlet and outlet temperatures.
- Cogeneration heat exchanger temperatures at inlet and outlet
- Room temperature.
- Cathode air flow rate.
- Air bleed flow rate.
- Inverter: active power, voltage, current, frequency, reactive power.
- Fuel cell: voltage, current and power.
- Stack's anode and cathode temperatures at inlet and outlet.
- Stack's anode and cathode pressures at inlet and outlet.
- Individual cell voltages

4 Diagnostic tests protocols

At ZSW, both EIS and cyclic voltammetry were performed once a week. 13 spectra were obtained in total.

4.1 Polarization Curves

Operating temperature was fixed at 65°C for all the experiments.
At FESB:

- Cathode is fed with air humidified at 83% (dew point temperature: 61°C) and pressurized at 1.5 bars. Two overstoichiometric ratios are used: λ=4 (1st& 2nd exp.) and λ = 2 (3rd exp).
- Anode is fed with humidified hydrogen pressurized at 1.5 bars with an overstoichiometric ratio of 2. Two humidification levels are used: RH = 83% (1st& 2nd exp.) and RH = 100% (3rd exp).

At FC Lab:

- Cathode is fed with fully humidified air at an overstoichiometric ratio of 3 and pressurized at 1.5 bars.
- Anode is fed with a fully humidify mixture of: 75% H_2 + 25% N_2 that is pressurized at 1.2 bars. Hydrogen overstoichiometric ratio is fixed at 1.5.

The polarization curves were performed according to the sequence presented in Table 6.

	FESB		FC Lab	
Step nr	j (A/cm²)	t_{step} (s)	j (A/cm²)	t_{step} (s)
1	OCV	20	1.1	
2	0.02 (3rd exp only)		0.99	900
3	0.04		0.88	
4	0.08		0.77	
5	0.12		0.66	
6	0.16		0.55	
7	0.2		0.44	
8	0.3		0.33	
9	0.4		0.28	
10	0.5		0.22	
11	0.6		0.17	
12	0.7		0.11	60
13	0.8		0.06	
14	0.9		0.02	
15	1		0CV	5
16	1.1		0.02	60
17	1.2		0.06	
18	1.3		0.11	
19	1.4		0.17	900
20	1.5		0.22	
21	1.6		0.28	
22			0.33	
23			0.44	
24			0.55	

25		0.66	
26		0.77	
27		0.88	
28		0.99	
29		1.1	

Table 6: Test steps for the polarization curve

4.2 Quick current sweeps

Quick current steps were performed at 65°C and an operating pressure of 1.5 bars. Reactant gases consisted in fully humidified air and hydrogen. Their respective inlet flow rates were fixed at 1 sL/min and 0.4 sL/min.
The sweep was done from 10 mA/cm² to 70 mA/cm², by steps of 3 mA/cm². Each step lasted 2s.

4.3 EIS

The experiments were performed at 65°C and 1.5 bars, and under 83% relative humidity (dew point temperature of 61°C). Air and hydrogen overstoichiometric ratio were respectively fixed at 4 and 2.
Impedance spectroscopies were recorded for three average current densities: 0.15A/cm², 0.25A/cm², 0.3 A/cm² (at ZSW) and 0.35A/cm² (at FC Lab). Frequencies ranged from 5012 Hz (at FC Lab) or 10 kHz (at ZSW) down to 0.1 Hz. The amplitude of the overimposed sinusoidal signal amplitude was fixed at ±10% of the average current density. Spectra were recorded with 10 points per decade in the frequency range of [5 kHz; 10Hz] and 5 points per decade for frequency range [10 Hz; 0.1 Hz].
The duration of an EIS for a 5 cells stack is around 20 minutes, and can be counted as 1 hour with the stabilization phases.

4.4 Cyclic and linear sweep voltammetries

All voltametries were performed under fully humidified hydrogen (at the anode) and nitrogen (at the cathode). The anode was both the counter and the reference electrodes while the cathode was the working electrode. The cells were operated at 65°C and 1.5 bars and the gases flow rates were fixed at 0.4 sL/min in both compartments.
Cyclic voltametries were performed between 0.1 and 0.6V vs RHE at a scan rate of 50 mV/s and replicated five times.
Linear sweep voltametries were performed between 0.1 and 0.5V vs RHE at a scan rate of 2 mV/s.

5 References

1. **ZSW.** Test Module 1.0: Durability Test. 2014.
2. **New Energy and Industrial Technology Development Organization (NEDO).** Cell Evaluation and Analysis Protocol Guideline (Electrocatalyst, Support, Membrane and MEA), PEFC Evaluation Project. 2014.
3. **ZSW.** Test Module 2.15: Polarization Curve. 2014.