Project Deliverable

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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 define tests protocol, characterization and measurement techniques for long duration term tests. According to the deliverable 2.3, a cycle is proposed. On one hand, at FCLAB, a 2000 hours duration test is a succession of daily cycles and then a succession of ten same cycles per day. On the other hand, accelerated test will start at FESB and ZSW. Furthermore, tests on the system will occur on Dantherm system.

ZSW provides stacks and the conditioning of them.

This deliverable presents the measurement techniques and their periodicity.

Keywords :

Experiment, protocol, measurement, fuel cell, characterisation

Revision History

Rev.	Date	Description	Author (Organisation)
0.1	Apr 30, 2014	Initial draft	Elodie Lechartier (FCLAB)
0.2	Apr 30, 2014	ZSW contribution	Merle Klages (ZSW)
0.3	Apr 30, 2014	DP Contribution	Alan Menard ((Dantherm)
0.4	June 6, 2014	FESB Contribution	Dario Bezmalinović (FESB)
1.0	June 13, 2014	Finalised layout, minor corrections	Federico Zenith (SINTEF)

Table of Content

1 Introduction

The deliverable presents the different tests protocols. Some long term tests (2000 hours) are scheduled at FCLAB on a 5-cell fuel cell supplied by ZSW.

Some accelerated ageing tests happen at FESB, on a single cell and ZSW, on a short stack. Finally, some tests occur on real system at Dantherm.

Depending on the possibilities of each partner, measures and protocols are defined for every trial type of ageing.

The measures should match and should be the most similar as possible, of sort to create a bigger data base for the developers of algorithms and for the PHM, as well as to propose a good reproducibility and generalization on the realized attempts.

Partner	Device	Test	Duration	Characterizations
FESB	ZSW: SCs and SS	Accelerated		IU every 7 days EIS at 3 current levels during IU
	BASF: 2 SC	Accelerated		Idem
ZSW	ZSW: SS	Accelerated		Idem
FCLAB	ZSW 2 SS	Durability	2000h (1 cycle/day), 2000h (10 cycles/day)	Idem
DANTH	µ-CHP system	Durability		

Table1 – Test schedule for all the partners (SC = single cell, SS = short stack, i.e. 5 cells)

2 Long duration term tests

2.1 Profile definition

The profile was defined with the agreement of all the partners. The profile is defined for allowing every partner to realize the same durability test with the same characterisations. There is a small difference in this profile that in the deliverable 2.3 for this aim: the lowest current density is 0.15 A/cm². Indeed, FCLAB is not able to do any EIS under 15 A.

The profile is given on Figure 1 and the different phases are explained in the Table 2.

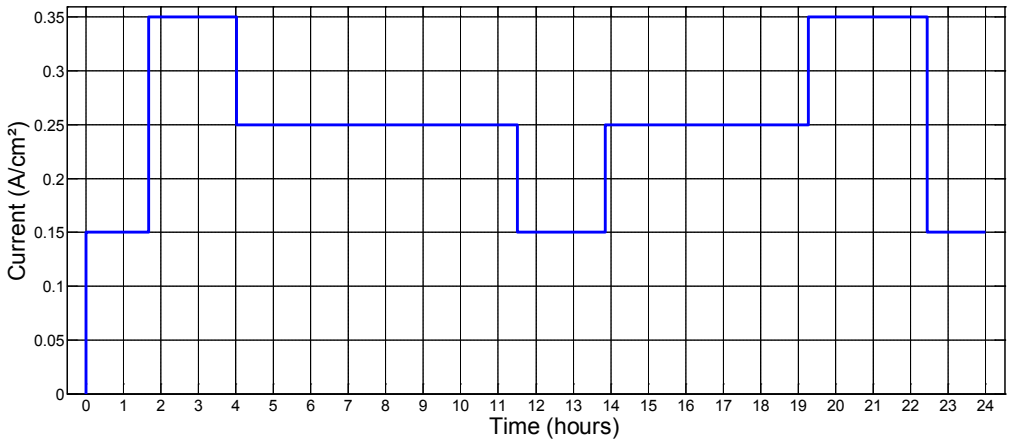


Figure 1 – Current profile of the test protocol

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 2 – Sequence of steps to perform endurance step

	Current Density (A/cm²)	Anode Stoic.	Cathode Stoic.
Max	**0.35**	1.3	2
Min	**0.15**	1.5	3
Mean	**0.25**	1.4	2.5

Table 3 – Current density and stoichiometry values to be used for endurance tests

However, in the profile, the steps will be done with ramps in order to avoid any damage to the fuel cell.

As defined in the deliverable 2.3, the duration of the durability tests will be 2000 hours. In FCLAB, the hours written on the profile will match with the real hours of the day. So if there is any trouble during the durability test, the profile will be started when it should be on the cycle, believing the time of the day.

The operating conditions can be found in the deliverable 2.3 and some are summarized below.

	Anode	Cathode
Inlet Composition	75 %H_2, 25% N_2	Air
Stoichiometry	1.3-1.5	2-3
Inlet Pressure (mbarg)	200	150
Inlet Temperature (°C)	60	60
Inlet Relative Humidity (%)	100	100

Table 4 – Operating parameters values for reactants

	Coolant
Inlet composition	100 % H_2O
Inlet Temperature (°C)	60
Outlet Temperature (°C)	70

Table 5 – Operating parameters values for coolant

2.2 Polarization curves

2.2.1 Post-conditioning polarization curve (cell and stack)

Polarization curve given by ZSW before stack conditioning

2.2.2 Protocol

The polarization curve protocol is described in [3]. Here, we consider the maximal load as 1.1 A/cm² and the nominal load as 0.66 A/cm².

The first step will be to reach 1.1 A/cm². If it is impossible to reach this value, the maximum point of the polarization curve will be the one that can be reached. When this maximum is reached, the current density is decreased stepwise to determine the descending polarization curve measured with decreasing electrical power output. The steps are recommended in accordance with table 4. If it is impossible to investigate both directions, the direction from higher current densities to lower current densities takes precedence.

In order to compare the results between the project partners, the step time is recommended to 15 minutes using a stability criterion of ±5 mV for the last 5 minutes based on the average cell voltage.

If shorter holding times are considered to be useful and provide similar results, the time may be shortened to e.g. 10 minutes. Thus, at least in the beginning of life a polarization curve with a relatively long holding time of 15 minutes should be recorded. It must be assured that shorter holding times do not affect the reproducibility during operation and assure comparability between results of the project partners.

At low current densities, under a minimum gas flow corresponding to 20 % of nominal, the hold time is reduced to 1 minute to avoid stack damage by dry out and/or degradation. For the same purpose, OCV hold time should be reduced to 5 sec.

Subsequently, the current density is stepwise increased to the maximum to determine the ascending polarization curve measured with increasing electrical power output (table 6).

step number	% of maximum current density	Current density (A/cm²)	
1	100	1,10	
2	90	0,99	
3	80	0,88	
4	70	0,77	
5	60	0,66	
6	50	0,55	15 min each point
7	40	0,44	
8	30	0,33	
9	25	0,28	
10	20	0,22	
11	15	0,17	
12	10	0,11	
13	5	0,06	1 min each point
14	2	0,02	
15	0	0,00	5 sec. at OCV
16	2	0,02	
17	5	0,06	1 min each point
18	10	0,11	
19	15	0,17	
20	20	0,22	
21	25	0,28	
22	30	0,33	
23	40	0,44	
24	50	0,55	15 min each point
25	60	0,66	
26	70	0,77	
27	80	0,88	
28	90	0,99	
29	100	1,10	

Table 6: Test steps for the polarization curve

The realization of the polarization curve will take 5 hours, 36 minutes and 5 seconds. That we can consider as 6 hours, as time for getting to the maximum and getting back to the next current density needed will take time.

If necessary for time reason, a few points (no more than 3 in the ascendant and 3 in the descendant) can be suppressed if needed; these points will have to be well chosen.

2.3 Electrochemical impedance spectroscopy

The EIS will be realized at the three different currents of the steps of the profile. It means, at:

- 0.15 A/cm²
- 0.25 A/cm²
- 0.35 A/cm²

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.

2.4 Characterization realization

The characterization phase is composed of (in order of realization):

1. A polarization curve (done as described in this deliverable)
2. The EIS at the lowest current density (0.15A/cm²)
3. The EIS at the middle current density (0.25A/cm²)
4. The EIS at 0.35A/cm².

Cyclic Voltammetry could be realised, if possible at the start and the end of the durability test. However, if this characterization technique could be realised around 500h and 1000h that would permit to draw the real evolution.

The characterization phase will be realised in one day between 8 AM and 7 PM every 7 days, the first one realised at t=0. The step at 0.15 A/cm² around noon won't be realised the day of the characterization.

The characterization phase will last around 9 hours, if everything goes well. It represents 5.4% of the profile, as a week is 168 hours.

3 Accelerated tests on single cell

Three different accelerated tests were performed on a single cell at FESB, namely:

1. OCV degradation
2. Potential cycling degradation
3. Degradation in simulated drive cycle

The goal of the above tests was to get some practical experience and understanding of underlying MEA degradation mechanisms.

All the experiments in the FESB laboratory were conducted on a single 50 cm2 cell using MEAs manufactured by BASF (12E-W MEA).

3.1 Profile definition

3.1.1 OCV degradation test

The experiment was conducted exactly according to the DOE AST protocol for the membrane chemical stability.

The test was conducted at steady state Opec Circuit Voltage (OCV) with the following conditions:

Tcell= 90 °C

CA: Air - 0.83 SLPM - 30% RH (DP = 61°C) - 0.5 barg backpressure

AN: hydrogen - 0.35 SLPM - 30% RH (DP = 61°C) - 0.5 barg backpressure

(flows correspond to stoichiometries of 5 at 0.2 A/cm^2)

The following diagnostic tests were performed after 0, 24, 48 and 60 hours:

- Polarization curve
- Quick current sweep
- Electrochemical Impedance Spectroscopy (EIS)
- Cyclic Voltammetry (CV)
- Linear Sweep Voltammetry (LSV)

3.1.2 Potential cycling degradation

The experiment was conducted in accordance with the DOE AST protocol for electrocatalyst degradation with some modification, with the following test parameters:

Cell in a “driven mode” (nitrogen on cathode; external source of power)

Profile: 30 seconds @ 0.9 V and 10 seconds @ 0.6 V with 50 mV/s ramp in ascending and 100 mV/s in descending direction. Total cycle duration 49 seconds.

Tcell = 80 °C

CA: nitrogen - 0.4 SLPM - 100% RH (DP =80°C) - 0.5 barg backpressure

AN: hydrogen - 0.4 SLPM - 100% RH (DP = 80°C) - 0.5 barg backpressure

The following diagnostic tests were performed after 0, 1000, 3000 and 5000 cycles (with additional CVs after 30, 100 and 300 cycles):

- Polarization curve
- Quick current sweep
- EIS

- CV (after 0, 30, 100, 300, 1000, 3000 and 5000)
- LSV

3.1.3 Degradation in simulated drive cycle

The experiment was conducted using slightly modified US06 drive cycle, with the following test parameters:

Load profile consists of 16 steps (total duration 300 seconds) and then it was repeated for 1500 cycles:

Step	mA/cm^2	duration (s)
1	0	15
2	200	20
3	400	20
4	20	12
5	200	18
6	400	18
7	20	15
8	200	20
9	400	20
10	20	12
11	200	20
12	SCAN	30
13	1000	20
14	800	30
15	20	10
16	400	20

Note: 4th, 7th, 10th& 15th step changed to OCV after 850 cycles to speed up the degradation.

Tcell = 65 °C, changed to 70 °C after 1000 cyclesto speed up the degradation.

CA: air - λ=2 - (DP =61 °C) 83% & 67% RH (after 1000 cycles) - 0.5 bargbackpr.

AN: hydrogen - λ=2 - (DP = 65 °C) 100% & 80% RH (after 1000 cycles) - 0.5 bargbackpr.

The following diagnostic tests were performed after 0, 300, 600, 1000, 1200 and 1500 cycles:

- Polarization curve
- Quick current sweep
- CV
- LSV

3.2 Diagnostic tests protocols

3.2.1 Polarization Curves

Tcell= 65 °C			
Cathode: air	λ=4 (1st& 2nd exp.) λ=2 (3rd exp.)	DP= 61 °C (83% RH)	0.5 barg backpressure
Anode: hydrogen	λ=2	DP= 61 °C (83% RH) 1st& 2nd exp. DP= 65 °C (100% RH) 3rd exp.	0.5 barg backpressure
Steps (1st& 2nd exp.) 20 seconds / step	OCV, 40, 80, 120, 160, 200, 300, 400, 500 ,…. 1600 mA/cm^2		
Steps (3rd exp.) 20 seconds / step	OCV, 20, 40, 60, 80, 100, 120, 140, 200, 300, 400, 500 ,…. 1600 mA/cm^2		

3.2.2 Quick current sweeps

Tcell= 65 °C			
Cathode: air	1 SLPM λ=10 @ 70 mA/cm^2	DP= 65 °C (100% RH)	0.5 barg backpressure

Anode: hydrogen	0.4 SLPM λ=16 @ 70 mA/cm^2	DP= 65 °C (100% RH)	0.5 barg backpressure
Recording procedure	10 – 70 mA/cm^2; 3 mA/cm^2/point; 2 sec/point → 1.5 mA/cm^2/sec; total 40 seconds		

3.2.3 EIS (conducted just for the first two experiments)

Tcell= 65 °C			
Cathode: air	λ=4	DP= 61 °C (83% RH)	0.5 barg backpressure
Anode: hydrogen	λ=2	DP= 61 °C (83% RH)	0.5 barg backpressure
Recording procedure	At 100 mA/cm^2; 0.1 – 5012 Hz		

3.2.4 Cyclic voltammetry

Tcell= 65 °C			
Cathode: nitrogen	0.4 SLPM	DP= 65 °C (100% RH)	0.5 barg backpressure
Anode: hydrogen	0.4 SLPM	DP= 65 °C (100% RH)	0.5 barg backpressure
Recording procedure	Anode counter & reference electrode; cathode working electrode Scan rate: 50 mV/s; 0.1 – 0.6 V; five measurements, the last one taken as representative Note: lower scan limit should be 0.05 V but it was impossible for us		

3.2.5 Linear sweep voltammetry

Tcell= 65 °C			
Cathode: nitrogen	0.4 SLPM	DP= 65 °C (100% RH)	0.5 barg backpressure

Anode: hydrogen	0.4 SLPM	DP= 65 °C (100% RH)	0.5 barg backpressure
Recording procedure	Anode counter & reference electrode; cathode working electrode Scan rate: 2 mV/s; 0.1 – 0.5 V; Value between 0.3 and 0.35 V is limiting current of H_2 oxidation (crossover)		

4 Accelerated tests on short stack

4.1 Profile definition

The chosen accelerated stress test (AST) procedure for short stacks will be derived from the DOE AST protocol for electrocatalyst, which includes cycling between 0.7 V and 0.9 V. An operation at open circuit voltage (OCV) is not investigated, as this can be easily avoided within the PHM system. Thus, for voltages below 0.9 V a degradation of the catalyst may be investigated with little influence on aging of the catalyst support. In addition, the chemical membrane aging should be minimized, as OCV is excluded.

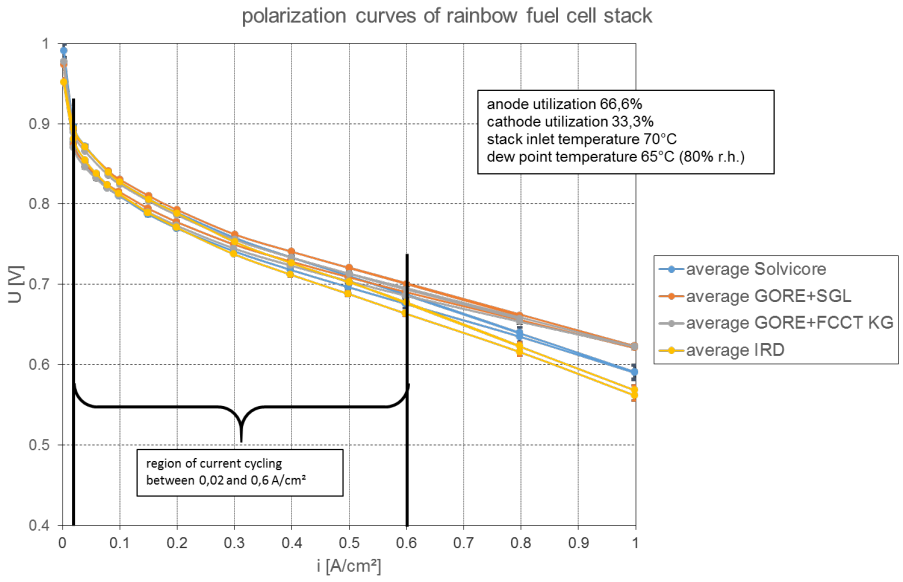


Figure 2 – Example for the choice of current densities according to voltage range for AST

Usually fuel cell stacks are operated in galvanostatic mode, while the DOE AST protocol represents a potentiostatic operation. In addition, being operated at constant potential can harm single cells with relatively poor performance compared to average cell voltage when applying an overall constant stack voltage. Thus, an operation in galvanostatic mode between two constant current levels based on the first polarization curve is chosen. That means, current densities are selected where all cells show a voltage between 0.7 V and 0.9 V (each value related to the best performing cells). Figure 2 gives an example for the choice of current density depending on a polarization curve in the beginning of life (BOL).

The single cell voltages will be cycled approximately between 0.7 V and 0.9 V. According to preliminary test results, the overall holding time at high voltage exhibits a higher probability of cell damaging then the holding time at low voltage level. According to the DOE protocol, the holding times will be set to 30 seconds. If no degradation is seen, the holding times at lower voltage level may be shortened, whilst the holding times at higher voltage levels are kept constant. Another preliminary measurement revealed that it is less important, if the voltage level is changed ramp- or stepwise as long as the holding times at stationary voltage levels are the same. Within a direct comparison, the total operating time was more dominant than the number of cycles.

The gas flow rates should be fixed to one value during the whole procedure corresponding to the flow at high current density (0.6 A/cm² for the given example). The gas stoichiometries are set according to table 3: 1.3 - 1.5 on anode and 2 - 3 on cathode. The original DOE protocol recommends nitrogen and hydrogen as supplied gases. Within this project, it has been decided to perform the tests in galvanostatic mode, since it was agreed upon performing accelerated ageing tests on a stack level using operating conditions which are approaching system operating conditions to the greatest possible extent. Moreover, performing this test with hydrogen/air in galvanostatic mode allows for a more precise adjustment of single cell voltages within the test compared to an external stack voltage adjustment combined with operation using hydrogen/nitrogen. This means, that air and simulated reformate should be used (see table 4).

The inlet gases into the fuel cell stack should be fully humidified (i.e. 100% r.h.) to avoid drying out.

The recommendation is to perform the accelerated test repeatedly for e.g. 20 h (i.e. 1200 cycles). Within the DOE protocol, the test is finished if the electrode ECA is decreases by 40%, the activity loss reaches 60% or performance is reduced by 30 mV at 0.8 A/cm².

4.2 Polarization curves protocol

Current voltage curves should be recorded after certain times (e.g. every week or more often, if severe changes during a 20 hours cycling test occur) during the AST procedure, but definitely before beginning AST and after end of life (EOL).

The polarization curves are performed as described in section 2.2.

4.3 Cyclic voltammetry protocol

The change of the catalytic activity can be compared in terms of electrochemical surface area (ECA). By cyclic voltammetry (CV), the current response of a fuel cell to a given voltage change can be analyzed. The cyclic voltammetry protocol is described in [3].

CV should definitely be done in the beginning of life and in the end of life. In addition, CV is performed after certain time intervals within the AST procedure. As the ECA is reduced significantly within the first cycles, CV should be performed more often during the first cycles corresponding to the rate of ECA reduction.

The CV is done at a minimum voltage of 50-100 mV. During preliminary CV measurements on larger fuel cell stacks equipped with varying catalyst layers and membranes, it was seen that strongly varying single cell resistances over the stack result in different voltage drops, while the voltage of the investigated cell follows the predefined profile of CV. This can cause harmful single cell voltages in some regions of the stack. For these conditions, the maximum single cell voltage during CV should be lowered to 0.6 V.

The integral of the upper area during hydrogen desorption will be used to calculate the ECA.

A voltage ramp of 30 mV/s is desirable. 3 cycles for one CV are recommended, calculating the average values of ECA with the last 2 cycles.

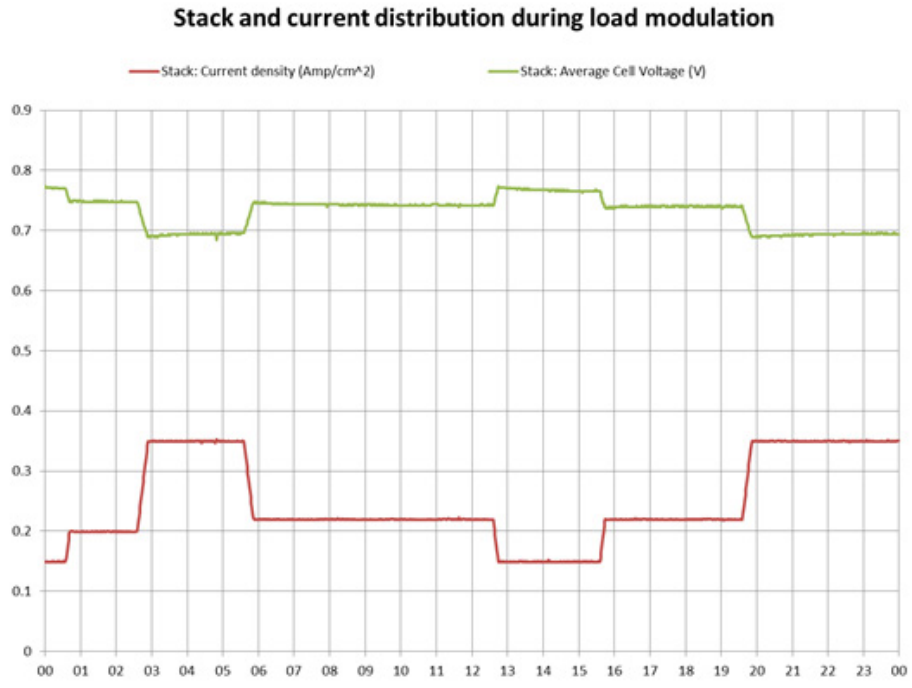
4.4 Electrochemical impedance spectroscopy

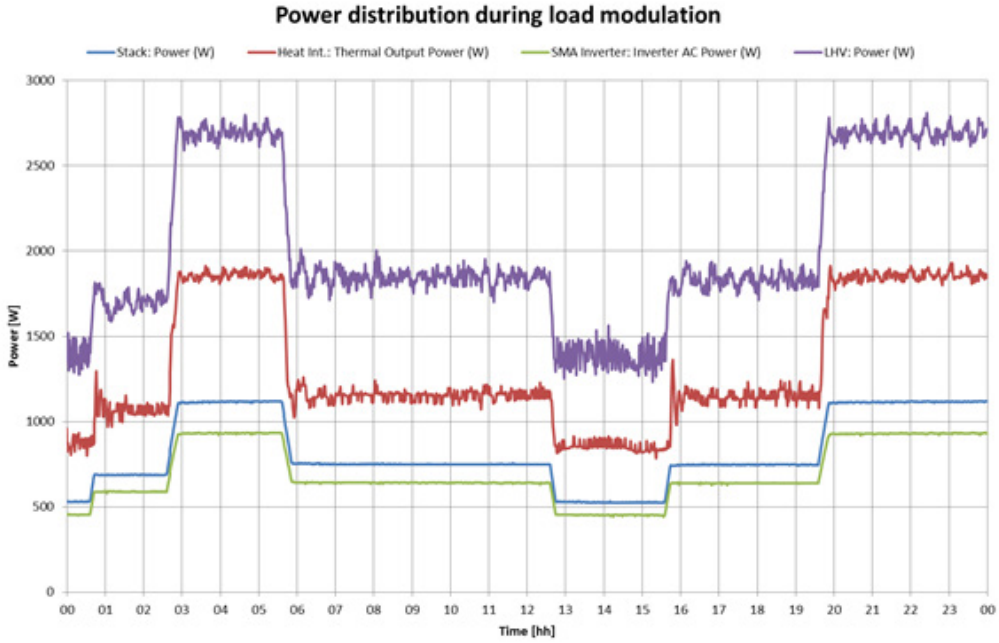
Electrochemical impedance spectroscopy is beneficial to be performed, but as time-consuming it may be reduced to important times in testing (i.e. BOL and EOL). The procedure is also described in [3].

5 Tests on Dantherm system

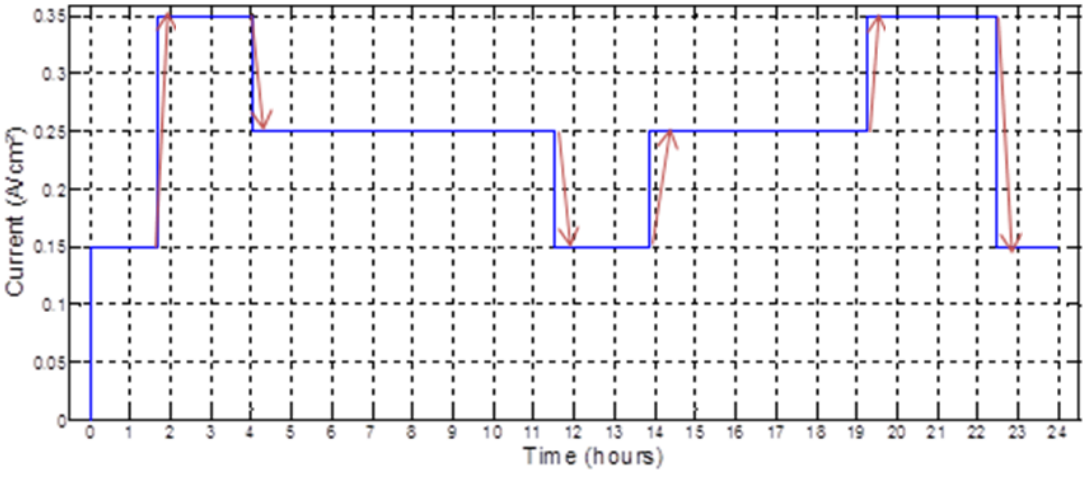
5.1 Profile definition

Dantherm has limited experience in load modulation on micro CHP system and performed some preliminary checks on one of our Micro CHP system available in the laboratory. The load profile has been tested on a EOL system and the results indicate that such a load profile can be applied. Unfortunately we have made a couple of errors in the transcript of the load profile described in 2.1, figure 1 which explain the load profile difference. However all three different current density were tested and performance were satisfactory as shown below.





Dantherm will therefore apply the load profile defined in the STACKTEST Project. We should note however that the system has a 20 mA/(cm².min) ramp rate and will follow the red arrows during load changes. This limitation is dictated by the thermal response of the reformer.



Dantherm's load profile from StackTest Project

The reactant stochiometries are controlled based on Ballard recommendation for 1030 V3 cogeneration stack for the cathode side. The anode stoichiometry will be govern by the thermal equilibrium of the system. Both stochiometries are automatically controlled.

acc. time	hold time	hold time	current density	anode stoic.	cathode stoic.
sec	sec	min	A/cm²	□fuel	□ox
0	3	0.05	0.00	∞	∞
3			0.15	1.3 -1.8	2.2
450	447	7.45	0.15	1.3 -1.8	2.2
450			0.15	1.3 -1.8	2.2
6060	5610	93.5	0.15	1.3 -1.8	2.2
6060			0.35	1.3 -1.8	1.8
14460	8400	140	0.35	1.3 -1.8	1.8
14460			0.25	1.3 -1.8	2.0
41460	27000	450	0.25	1.3 -1.8	2.0
41460			0.15	1.3 -1.8	2.2
49860	8400	140	0.15	1.3 -1.8	2.2
49860			0.25	1.3 -1.8	2.0
69360	19500	325	0.25	1.3 -1.8	2.0
69360			0.35	1.3 -1.8	1.8
80760	11400	190	0.35	1.3 -1.8	1.8
80760			0.15	1.3 -1.8	2.2
86400	5640	94	0.15	1.3 -1.8	2.2

5.2 Polarization curves protocol

The system will operated according to the load profile defined in 5.1. No polarisation will be performed at system level.

5.3 Electrochemical impedance spectroscopy protocol

EIS measurement would not be performed at system level since we are not equipped to perform such measurement.

5.4 Other measurements

The following outputs will be measured as part of the standard system.

T19	Stack coolant In temp	PT1000	60°C
T18	Stack coolant Out temp	PT1000	70°C
T26	Cogen middle temp	PT1000	59-63°C
Thxo	Cogen heat echanger OUT temp	PT1000	60-65°C
Thxi	Cogen heat echanger IN temp	PT1000	25-40°C
Tct	Cabinet temp	PT1000	40-50°C

MFM-8	Cathode air flow meter	1-5VDC - 0-70NLPM
MFM-9	Air bleed flow meter	1-5VDC - 0-2NLPM

Enable FC switch	ManOpMode_CAN
Bleeder Resistor 60Ω - inverter	FCDisChg_CAN
Inverter Active Power	InvPwrAt_CAN
Inverter Voltage	InvVtg_CAN
Inverter Current	InvCur_CAN
Inverter Frequency	InvFreq_CAN
Inverter reactive power	InvPwrRt_CAN
Low voltage bridge Power	HvDcVtg_CAN
High voltage bridge Power	LvDcVtg_CAN
FC voltage	FcVtg_CAN
FC current	FcVtg_CAN
FC power	FCcPwr_CAN

The additional measurements are fitted to the system:

Stack cathode Inlet temp	PT1000	60-70°C
Stack cathode Outlet temp	PT1000	60-70°C
Stack Anode Inlet temp	PT1000	60-70°C
Stack anode Outlet temp	PT1000	60-70°C
Cathode inlet pressure		0-250mbar(g) 4-20 mA signal
Cathode Outlet pressure		
Anode inlet pressure		
Anode outlet pressure		
Cell voltage monitoring		47 channels multiplexer

6 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.

[4] ZSW, *Draft_TestModules 2.18, Ch. 11.5,* Ulm, 2014.