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Advanced Electrolyser for Hydrogen Production with Renewable Energy Sources

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Definition of the ADEL testing protocol and revised test matrix

WP 1. – Stack Components optimization for durability and robustness

Deliverable D1.5

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Glossary

EC	European Commission
FP7	7th Framework Programme
GA	General Assembly
ADEL	Advanced Electrolyser for Hydrogen Production with Renewable Energy Sources
WP	Work Package
SoA	State-of-the-Art

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Introduction

A provisional protocol (deliverable D1.4) has been defined at the beginning of the project in order to start promptly the first test campaign with SoA components. Cells, SRUs and stacks have been tested following this protocol and main results are detailed in deliverable D1.1.

In parallel, WP2 has specified some recommendations for the ADEL protocol presented in this deliverable, based on operation constraints happening with the coupling of an intermediate temperature electrolyser (ITSE operating at ~ 700 °C) with renewable energy sources.

The ADEL protocol targets the technical parameters established for covering the project objectives of getting an efficient ITSE, durable and flexible enough for operation under load from 0 to 100% of its maximal power.

To ensure consistency between results obtained at the cell, SRU and short stack levels by the testing partners, the first test matrix established in deliverable D1.4 has been revised according to the ADEL protocol here defined.

As for the provisional test protocol (deliverable D1.4) special attention is paid to the standardization of operation conditions (start-up, electrochemical characterization) and data collection between the testing partners in order to achieve efficient data collection and comparison.

Achievements of the first test campaign with the provisional test protocol (cf. deliverable D1.1)

Among the three test schemes defined in the provisional test protocol, the first one dedicated to single cell tests and consisting in j-V measurements at three operating temperatures and for two inlet humidities of 50 vol.% and 90 vol.% steam has been entirely followed. Performances of SoA SP cells with LSCF O_2-electrode have been compared with ECN cells with LSC O_2-electrode (results are discussed in deliverable D1.1):

- ✓ for SoA SP cells, operation conditions recommended are first the use of LSC current collecting layer on the O_2-electrode side, then operation temperature of 750 °C for achieving a reasonable current density at the thermal neutral voltage and finally under typical SOEC operating conditions of 90%H_2O/10%H_2 | air.
- ✓ for ECN cells, operation at 700 °C with high current density (-1.3 A/cm^2) at the thermal neutral voltage has been demonstrated under typical SOEC operating conditions of 90%H_2O/10%H_2 | air.

Based on these single cells results, the second test scheme defined in deliverable D1.4 (ref. Table 2) has been followed for SRUs measurements. Durability test of an SRU with an ECN cell has been carried out at 700 °C and 90%H2O/10%H2 | air. Measured ASR is about 0.36 Ω cm^2 and a current density of -1.15 A/cm^2 is achieved at the thermal neutral voltage for a steam conversion rate of 74%. Durability test also shows that degradation is a major issue with 2%/kh degradation rate measured at -0.5 A/cm^2 and 700 °C. The same protocol was used for TOFC short-stack integrating ECN cells. Durability test of about 2000 h at 700 °C was performed showing for the best SRU an area specific

resistance of 0.4 Ω cm^2 at -0.6 A/cm^2 (U ~1.125 V). The overall stack degradation amounted 4.3 %/1000 h or 1.5%/1000 h without the worst SRU. SOFCPOWER stacks with SP cells were also tested. However, the insufficient gas-tightness prevented reliable characterization of the durability of the stacks. From the performance point of view, operation at 750 °C is also recommended in order to obtain a current density of above |-0.5| A/cm^2 at the thermal neutral voltage.

During the first test campaign, first and second test protocols dedicated to performance and durability evaluation of cells, SRU and stacks under steady state conditions have been fulfilled. The third test protocol (deliverable D1.4, Table 3), for analysing the behaviour of cells, SRUs and stacks under transient operation conditions has been entirely followed at the SRU level and only partially realised with the TOFC stack integrating ECN cells. With this stack 756 operation cycles (current ON/OFF cycling between 0 (OCV) and -0.6 A/cm^2 (thermal neutral voltage) were realised corresponding to test a) and test b) of the third test protocol. Results indicate that it could be possible to modulate the load of the stack without additional degradation for following renewable electricity production. However, voltage fluctuations probably due to unstable contact in the stack forced to stop the experiment without doing test c) corresponding to cycle between OCV and exothermal mode (~1.5 V). At SRU level, results were similar to the stack ones for test schemes a) and b). Additional degradation was observed when cycling between OCV and 1.5 V.

ADEL testing protocol

The ADEL testing protocol aims at measuring performance and durability of optimized materials for cells, SRUs and stacks under steady-state and transient operation conditions. Experiments should be close to operation conditions with power loading happening when coupling the electrolyser with renewable energy sources. In that sense, a description of renewable energy conversion technologies (converting solar energy and wind energy to electricity) has been done in deliverable D2.2 of WP2. Strategies for powering ITSE units with renewable electricity have been proposed in deliverable D2.4 aiming at defining operation constraints for the electrolyser. Three major operation constraints were identified for operating ITSE unit with variable energy sources (ref. deliverable D2.5):

*Flexible load operation from 0 to 100% power (or ~120% if the thermal neutral voltage is used to define the maximum power of the electrolyser)

*Plateau duration

*Speed rate for switching from one current density to the other

Experiments corresponding to these operation constraints have been identified and are detailed in the present deliverable.

Steady-state operation of cells, SRUs and short-stacks

Table 2 from deliverable D1.4, describing test scheme for operation under steady-state conditions has to be done with optimized cells, SRUs and stacks materials, in order to be directly comparable with SoA materials. Expected results are the increase of performance and the reduction of degradation at the single cell, SRU and short –stack levels. Composition of inlet gas to the hydrogen electrode is 90 vol.% H_2O and 10 vol.% H_2. For steps B and C the flow rate considered is the one defined in guideline page 11, i.e. total flow rate is 12 $Nml/min.cm^2$ decided to be able to reach 60% of steam-to-hydrogen conversion rate (SC) at about -1 A/cm^2. However, for the durability measurement on step D, the flow

rate has to be reduced to operate at the thermal neutral voltage with a steam-to-hydrogen conversion rate at least equal to 50%.

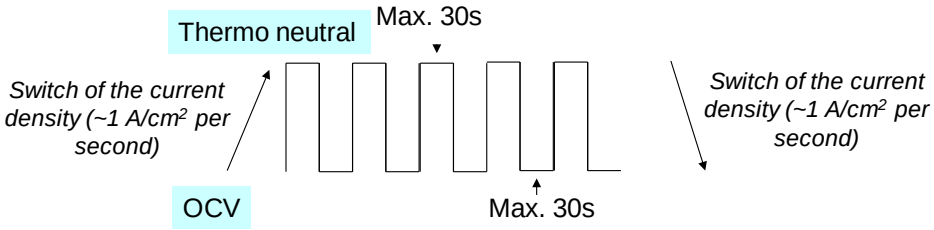
Table 1: Table 2 from deliverable D1.4 - Test protocol for the determination of degradation under steady-state conditions at single cell, SRU and short-stack levels.

Durability test at 700°C and cell voltage close to the thermal neutral voltage				
Sealing and hydrogen electrode reduction				
A	Gas feeding	90 vol. % H_2O (H_2 10%)	OCV	~30 min
B	j-V curve	90 vol.% Hum (H_2 10%)	j-V curve up to j_{max} levelling off the cell voltage	~20 min
C	EIS	90 vol. % Hum (H_2 10%)	EIS = f(0.0, -0.2, -0.4, -0.6, -0.8 etc.)	~60 min
D	Durability test	90 vol.% Hum/10 vol.% H_2, Min. SC= 50%	V = f(time) Current density corresponding to $V_{thermoneutral}$ for starting the test	1000 h for single cells, SRUs and short-stacks
E	j-V curve	90 vol.% Hum (H_2 10%)	j-V curve up to j_{max} levelling off the cell voltage	~20 min
F	EIS	90 vol. % Hum (H_2 10%)	EIS = f(0.0, -0.2, -0.4, -0.6, -0.8 etc.)	~60 min

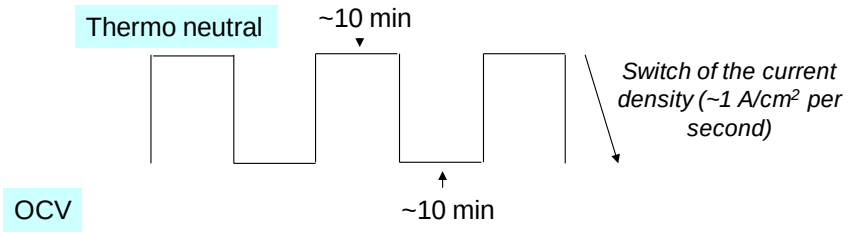
Transient operation of single cells, SRU and short-stacks

Table 3 from deliverable D1.4 integrates three test schemes for measuring performance and degradation of cells, SRUs and short-stacks under transient operation conditions:

a) Influence of electric cycles under cell voltage limited to the thermal neutral value



b) Influence of electric and thermal cycles with cell voltage limited to the thermal neutral value



c) Influence of electric and thermal cycles switching from endothermal to exothermal operation.

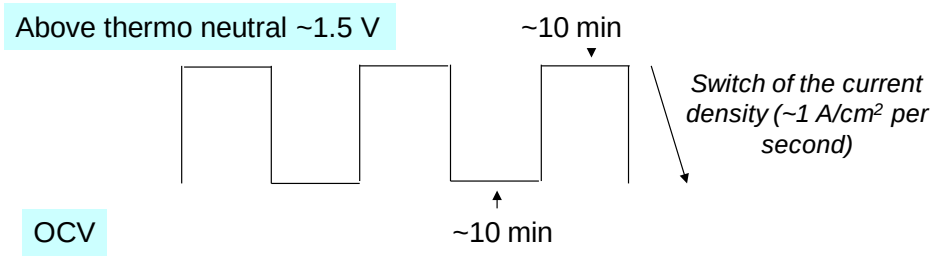


Figure 1: Cell voltages cycling from OCV to either thermo neutral, or exothermal mode of operation with two duration plateaus, i.e. 30 seconds and 10 minutes.

Test results of SoA materials following these test schemes indicated that tests a) and b) did not affect the cell behavior (performance and degradation) neither at cell level nor at SRU and short-stack levels. The same result was measured with the SRUs for test c). To simplify and reduce the number of test schemes the ADEL test protocol will not include the test a) which did not affect cell performance and lifetime. Test schemes b) and c) are conserved for comparison between optimized materials and reference ones.

Flexible load operation

Tests b) and c) of the third test protocol described in deliverable D1.4, are adapted for studying the capability of the stack to modulate its power. Test c) was partially realized during the first test campaign for reasons explained previously. It consists in cycling the cell voltage from OCV to cell voltage above the thermal neutral voltage (even close to 1.5 V when feasible). The test will be done in the galvanostatic mode of operation at OCV for the minimum value and for the maximum value close to $V_{thermal\text{-}neutral}$.

According to the results of the first test campaign, SoA SP cells have to operate above -0.5 A/cm^2 (750°C) for getting exothermal conditions. A higher current density is required with ECN cells for achieving same operation conditions (above -1 A/cm^2 at 700°C). Higher current density at similar voltage is expected with optimized SP cells which may lead to modify Figure 2.

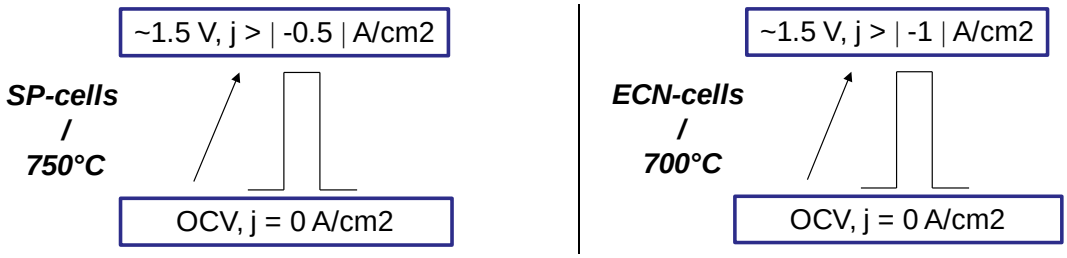


Figure 2: Current density for operating exothermally SoA cells from SP at 750°C and ECN at 700°C.

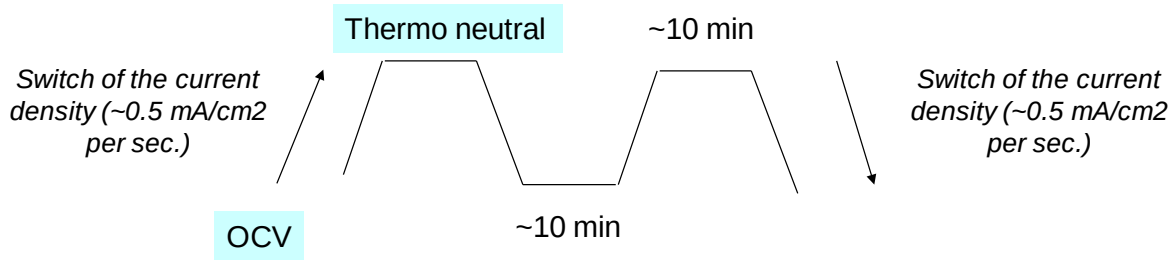
The evolution of the cell voltage will be recorded as function of the time. **In case of a cell voltage increase by more than 0.05 V compared to the initial value,** it is suggested leaving the device under steady-state conditions at the current density used for the durability test (Table 1) to see whether the cell voltage is stabilising at its previous value (i.e., to evaluate whether it is passivation or degradation of the cell). **10 to 12 h of stabilisation is recommended.** After cell recovery, the test is restarted. Experiment duration of about 5 days is suggested.

Speed or switching from one current density to the other

Value of the speed rate for switching from OCV to voltage above thermal neutral voltage was defined as 1 A/cm^2 per second in the previous test protocol. Fast speed current density change is corresponding to ON/OFF operation of the electrolyser (see deliverable D2.5), described in Figure 1.

Other possibility for operating the electrolyser is to follow load curves of renewable electricity production. A lower speed of current change of 0.5 mA/cm^2 per second is thus proposed corresponding to about 30 minutes from OCV to cell voltage above the thermal neutral voltage. As for tests at 1 A/cm^2 per second two tests are proposed corresponding to two maximum cell voltages: thermal neutral and above thermal neutral (~1.5 V) (Figure 3).

a) Influence of electric and thermal cycles with cell voltage limited to the thermal neutral value



d) Influence of electric and thermal cycles switching to exothermal operation.

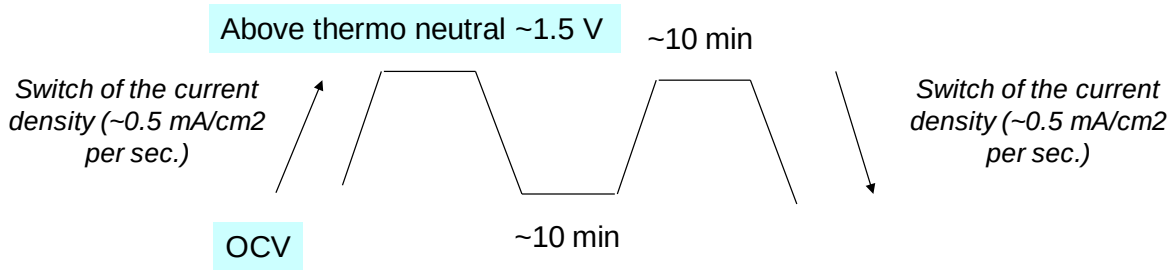


Figure 3: Cell voltages cycling from OCV to either thermo neutral, or exothermal mode of operation with a duration plateau of 10 minutes at each voltage. Speed for switching the current density is 0.5 mA/cm^2 per second.

Summary

Table 2 describes the sequence of the tests previously described. For cells, SRUs and short-stacks the testing protocol starts with 1000 hours electrolysis under steady state conditions at current density corresponding to the thermal neutral voltage. According to the degradation measured two possibilities are proposed:

1) The degradation of the cell voltage is below 8% (cell voltage below 1.4 V after 1000 hrs operation). The next test to be done is the test under transient operation condition between OCV and thermal neutral voltage after adjusting the current density to the thermoneutral voltage (steps D1 & D2)

2) The degradation of the cell voltage is above 8% (cell voltage above 1.4 V after 1000 hrs operation). The next test to be done is the test under transient operation between OCV and exothermal voltage (steps D3 & D4) because reduce the current density for operating between OCV and thermal neutral voltage is not relevant for evaluating the degradation due to the transient conditions of operation.

Table 2: Sequence of tests of the ADEL testing protocol

Step #	Definition	Hydrogen electrode gas composition	Test	Duration[1]
Sealing and hydrogen electrode reduction				
Test start-up				
	OCV stabilisation at 700°C	Humidified H_2 (0 to 10 vol.% H_2O)	OCV	~30 min
Fuel Cell Mode				
A	Fuel cell mode	Humidified H_2 (0 to 10 vol.% H_2O)	j-V curve up to j_{max} levelling off the cell voltage	~20 min
A	Fuel cell mode	Humidified H_2 (0 to 10 vol.% H_2O)	EIS = f(0.0, 0.2, 0.4, 0.6, 0.8 etc.)	~60 min
Durability under Steady state and Transient operating conditions				
Durability Test				
B1	Change of humidity and stabilisation	90 vol. % Hum (H_2 10%)	OCV	~30 min
B2	j-V curve	90 vol. % Hum (H_2 10%)	j-V curve up to j_{max} levelling off the cell voltage	~20 min
B3	EIS = f(j)	90 vol. % Hum (H_2 10%)	EIS = f(0.0, -0.2, -0.4, -0.6, -0.8 etc.)	~60 min
C	Durability test	90 vol.% Hum/10 vol.% H_2	V = f(time) Current density corresponding to $V_{thermoneutral}$ for starting the test	1000 hrs
B2 → B3				
Transient operation between OCV and thermal neutral voltage				
D1	Load cycling	Switch of j (~1 A/cm^2 per second scan rate) with stabilisation plateau of 10 min at each current density	Cycles between OCV and **Ucell = U thermal neutral** Measurement of V = f(time), T_{outlet} =f(time)	~5 days
D2	Load cycling	Switch of j (~0.5 mA/cm^2 per second scan rate) and stabilisation plateau of 10 min at each current density	Cycles between OCV and **Ucell = Uthermal neutral** Measurement of V = f(time), T_{outlet} =f(time)	

[1] Duration is a rough estimation for resource planning only. Values will depend on test results and test behaviour.

B2 → B3				
Transient operation between OCV and exothermal voltage				
D3	Load cycling	Switch of j (~1 A/cm^2 per second scan rate) and stabilisation plateau of 10 min at each current density	Cycles between OCV and **Ucell > $V_{thermoneutral}$** Measurement of V = f(time), T_{outlet} =f(time)	~5 days
B2 → B3				
D4	Load cycling	Switch of j (~0.5 mA/cm^2 per second scan rate) and stabilisation plateau of 10 min at each current density	Cycles between OCV and **Ucell > $V_{thermoneutral}$** Measurement of V = f(time), T_{outlet} =f(time)	~5 days
B2 → B3				

Further guidelines

Heat-up and initial operation:

Cell heat-up is done under argon or nitrogen flowing along the electrodes. The temperature rise to the hydrogen electrode reduction temperature occurs with a 60°C/h ramp. Then the hydrogen electrode reduction is realised according to partners' procedure (see deliverable D1.4).

After reduction, the cell temperature is set to 700°C. Once the temperature has stabilised, the flow to the oxygen electrode and the hydrogen electrode are increased to 12 Nml/min.cm^2 in steps of 5% of the total flow rate every 30 seconds. The total flow rate to the hydrogen electrode (steam + hydrogen is required) has been decided to be able to reach 60% of steam-to-hydrogen conversion rate (SC) at about -1 A/cm^2. It was previously observed that depending on the porosity and thickness of the H_2 electrode some cells are limited by the gas diffusion at a SC below this value. Consequently, it is important for each category of cells to define the maximum steam-to-hydrogen-conversion rate achievable before reaching the diffusion limitation. Based on these results, the long term measurement of cells, SRUs and stacks can be designed to avoid operation limited by gas diffusion at the hydrogen electrode side.

Once the hydrogen and oxygen electrode flow rates are established, the OCV of the cell is recorded to check the sealing quality of the SRUs and stacks. The test starts by operation in fuel cell mode with a gas inlet composition to the hydrogen electrode composed of dry or humidified hydrogen. After the measurements of the j-V curves and of the electrochemical impedance spectroscopy (EIS), the current direction is reversed to operate in electrolysis mode. Steam is supplied to the hydrogen electrode starting with a gas composition of 90 vol. % steam and 10 vol.% hydrogen for the SRUs and stacks (step B1 – Summary table) while the total flow rate is kept at 12 Nml/min.cm^2. This step is realised at OCV.

The humidified gases are supplied to the cathode via the humidification system (described in the next section). To reach a new composition, the concentration of hydrogen is decreased by 10 vol. % every 30 seconds while increasing the steam flow rate and thereby keeping the total flow rate constant.

After stabilisation of the cell voltage close to OCV, a j-V measurement is performed followed by an EIS measurement. If possible, H_2 production (outlet) would be measured in order to check Faraday's law and also tightness. A common data format for EIS presentation is useful for comparison and exchange of data between the project partners, such as the one used by ZView from Scribner (Table 4) (ZView operation does not require a hardware dongle, unlike the operation of the measurement software ZPlot).

Table 1: Common data format for comparison.

Frequency (Hz)	Time	Z' (Ω.cm^2)	Z" (Ω.cm^2)
	(optional)		

Spectra recording is done by a stepwise decrease of the current from 0 A/cm^2 to -0.2 A/cm^2, -0.4 A/cm^2, and so on, until -1.0 A/cm^2 or until the limit of the cell voltage (e.g., given by a gas diffusion limitation or reduction potential of the electrolyte) is achieved. The complete j-V curve consists of scans in both directions; it starts with the scan into the negative current direction. Current-voltage curves are taken as full cycles, i.e., in most cases starting at zero current, going to the maximum

current magnitude and back to zero. Only after long term operation under constant current it is preferable to start at the nominal DC current and to go back to this value. This test is carried out once the cell voltage has stabilised, which means that the OCV variation, corrected for eventual cyclic variations arising from gas/steam mixer artefacts, has dropped below 2 mV in 5 minutes.

Cooling down

The steam supply is cut and the concentration of hydrogen is decreased by 5% of the total fuel flow rate every 30 seconds while increasing the nitrogen flow rate, keeping the total flow rate constant. The humidifier is cooled to room temperature. The final composition should be nitrogen and 5-9 vol. % hydrogen. Then, the temperature decrease is set to 60°C/h.

Recording of current-voltage curves (j-V curves)

The j-V measurements under galvanostatic control are recorded as well as if possible, the variation of the temperature of the cell or stack during the j-V measurement. Automatic continuous recording is recommended with a scan rate of about 0.05 to 0.1 A/cm^2 per minute. If this is not possible, a stepwise recording can be done, with current step increments of 0.05 A/cm^2 every 30 s. A minimum magnitude value of the current density of -1 A/cm^2 is targeted; the actually recorded maximum value may be limited by, e.g., a gas diffusion limitation, reduction potential of electrolyte or by equipment limitations.

Impedance Spectroscopic (EIS) measurements:

Impedance spectra are realised applying an AC current < 50 mA/cm^2 in the frequency range from 10^4 Hz (or higher, if feasible) down to about 10^{-2} Hz. The spacing of the data points in frequency should be at least 5 (preferably 7 or more) points per frequency decade, starting the measurement at high frequency. Cycle repetition for noise reduction and improvement of the data quality may be required, at the cost of a decrease of the measurement speed, if also done for the data at lower frequencies. A low electrical noise level and a stable humidification should allow the setting of integration times in the order of 1s per point, which means cycle averaging only for higher frequencies than 1 Hz (one full cycle is the minimum time required for a measurement). A full spectrum can then be completed in around ten minutes. If significant noise occurs in the 0.01 to 1 Hz range (which may notably come from the humidification system) cycle repetition may be required also at the lowest frequency data, causing much longer measurement times. Alternatively, the AC current modulation may be increased, if possible from signal-linearity considerations. The quality and consistency of the data collection is let under the responsibility of testing partners (e.g. KK transforms, additional frequencies sweeping, and so on) keeping in mind the time schedule for each test (see testing timetable).

Humidification system

The water is supplied continuously to the evaporating system. Considering a cell of 100 cm^2 active surface area and the gas flow in the hydrogen electrode of 12 $Nml/min.cm^2$ as proposed previously, the maximum water flow required is 52 g/h to achieve 90% H_2O/10 % H_2. That means a maximum steam flow of 100 g/h is sufficient for a proper operation. For short stack test, the range of the humidifier should be adapted accordingly.

Testing timetable

The second test campaign based on the ADEL testing protocol previously described will consist of the tests of improved single components that will have fulfilled the ADEL specification threshold and that will be integrated in SRUs and, in selected cases, in short stacks. Improved components selected are listed in the Table 3.

Table 3: selected improved components to be tested in the second test campaign

Testing partner / Tested component	**Components**	**CEA**	**JRC**	**HTc**	**EIFER**
Single cell	SP CSC Ni-YSZ/YSZ/GDC-LSC40	X	X		
	SP CSC Ni-YSZ/YSZ/GDC—$Pr_2NiO_{4+\delta}$-LSC40	X	X		
SRU	Interconnects: Crofer 22 APU	X			
	ECN and/or SP cells	X			
	Sealing : Schott G018-311	X			
	Coatings	X			
Short-stacks	2G SP cells SP design			X	X
	2G SP cells TOFC design				X

Table 4 below indicates the test benches availability of the different testing partners for the year 2013, last year of the project. According to that table partners responsible for the delivery of the components can planned components manufacturing and sending to each testing partners.

Month	Week	CEA		JRC	HTc		EIFER	
		Single cells	*SRUs*	*Single cells*	*Single cells*	*Short-stacks* **2 short-stacks from SP*	*Short-stacks* *2 short-stack from SP *2 short-stacks from TOFC	
						Test bench N°2	SP short stacks (Test bench N°3)	TOFC short stacks (Test bench N°5)
January	1					ECN cells SP Conclusion of transient tets	*SoA cells SP (last campaign)*	
	2							
	3							
	4							
February	5		2G SRU with an ECN cell and LNF as collecting layer Durability in steady state and transient conditions					*TOFC stack with SoA cells from SP (last campaign)*
	6							
	7	2G SP cells Performance 2G SP cells Durability in steady state conditions				Start-up 1st 2G short-stack	Start-up 2G short-stack	
	8							
March	9							
	10							
	11							
	12							
April	13							
	14							
	15							
	16					End experiments		
	17						End of the experiment	
May	18							
	19							Start-up 2G TOFC short-stack with SP cells

	20					Start-up 2nd short-stack	Start-up 2G short-stack	
	21							
June	22							
	23							
	24							
	25							
July	26							
	27							End of the experiment
	28							
	29					End of experiments		
	30							
August	31						• **Longer duration or other experiments** • •	Start-up 2G TOFC short-stack with SP cells
	32							
	33		2G SRU with 2G SP cells if relevant Durability in steady state and transient conditions					
	34						End of the experiment	
September	35							
	36							
	37							
	38							
October	39							End of the experiment
	40							
	41							
	42							
	43							

November	44							
	45							
	46							
	47							
December	48							
	49							
	50							
	51							
	52							