Reversible solid oxide Electrolyzer and Fuel cell for optimized Local Energy miX

Cells and Stacks testing protocol
Deliverable D2.1

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Abstract

This document describes the experimental protocols for solid oxide cell and stack testing, including electrochemical performance tests and long term tests. The long-term tests include steady-state operation and reversible (rSOC) cycling tests.

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1. Introduction

The main objective of cell and stack testing is to quantify improvement of cell/stack performance that results from the optimization process performed in the frame of REFLEX project. By performance it is understood electrochemical performance and durability performance, including durability under daily cycling between SOEC mode and SOFC mode representative of the in-field operation.

Development and characterization are two main aspects of the process that lead to the goal and one can say that final objective will be reached once three main tasks, related to testing activities, will be achieved:

1) Validate the cell developments and optimizations done by Elcogen, with various generations of cells. This will be done at DTU several times during the whole project as often as a new cell is ready from Elcogen. The aim of this kind of test is to quantify electrochemical performance and give, in a time as short as possible, any information about cell ability to be operated at Reflex project target of (i) current density, (ii) voltage, and (iii) durability. This for finally identify among all the tested cells those that seem to be the most appropriate for integration into stacks and modules for in-field operation.

2) Perform durability test in rSOC conditions representative of in-field operation at cell scale. This has to be performed once at the beginning of the project to quantify a reference state, and as soon as the most promising cells will be identified to quantify improvement achieved during cell development task. DTU is in charge of this part.

3) Perform durability test representative of in-field operation at SRU, and short or real stack scale. As for cell scale this kind of test has to be performed twice, firstly using the cells corresponding to the state of the art at the beginning of the project, secondly with cells that give the best results at due time, according to the whole project planning, to start the cell serial production for stack manufacturing. The stack scale testing will be mainly conducted by CEA, with some DTU contribution at SRU scale.

   Notice that cell development could be continued after serial production launching.

The following text presents the results of interactions, between Reflex Work Package 2 partners, on cell and stack testing topic that are synthesized in two main sections presenting respectively cell and stack testing protocols.

Two preliminary remarks have to be done:

1) As electrolysis is proved to generate more degradation for the cell, the presented protocols emphasize on this mode of operation. After cell optimisation process, a revision of testing protocols, that could not be specified yet, will certainly be necessary to quantify the optimised performances in both operating modes.

2) It is obvious that development activities will generate observations and questions not identified yet that will, most likely, lead to adjust testing protocols to improve the global efficiency of the testing task. Consequently the presented protocols have to be understood as guidelines, and a detailed and exhaustive description of actual protocols will be absolutely necessary in test reporting documents to know what was really done during tests.

2. Cell testing protocol

Cell testing task can be represented by a flow chart including three steps as shown in Figure 1. During the first step, a cell is heated up, reduced and conditioned. Then intrinsic electrochemical performances are measured. Finally long term tests will give trends on degradation under rSOC cycling conditions.

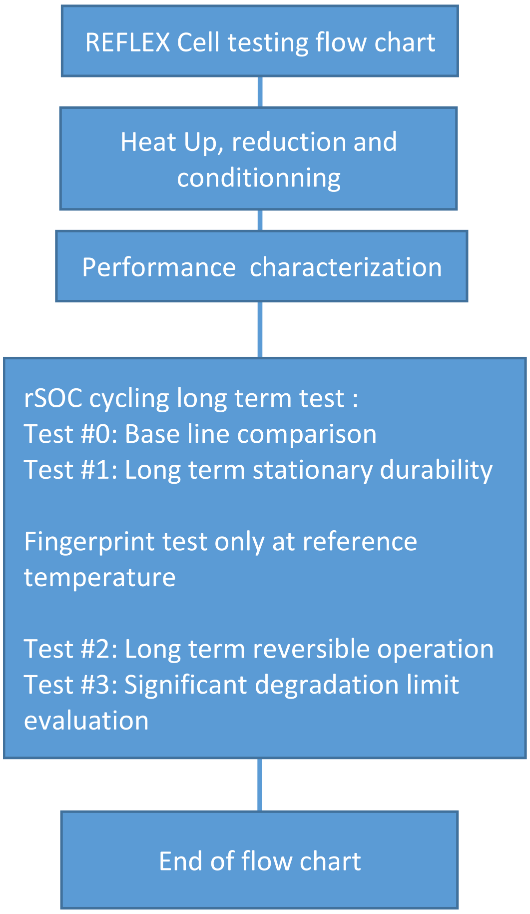


Figure 1: Cells testing task flow chart

2.1 Cells samples

To characterize cell performances at the beginning of the project, Elcogen has shipped a sample of ten cells to DTU. The cells consist of porous anode contact layer, anode diffusion layer with variable thickness and microstructure for different types of cells, anode active layer, thin electrolyte, barrier protective layer and cathode.

Cell type	Number	Number devoted to	
		Performances tests	Long term tests
530 B	2	2	
400 B HM	2	2	
400 B SM	4	2	2
300 C	2	2	

Table 1: Tested cells sample

Table 1 details tested cells type, as well as number of cells delivered by ELCOGEN to DTU for cells testing task.
Four different type of cells will be evaluated. Cell type number precise thickness of half cell in microns, while letters "B" and "C" are used for different substrate microstructures. "SM" and "HM" abbreviations are used internally at Elcogen for different materials used in production of anode diffusion layer. For each type, two cells are delivered for each planned test (to cover any failure).
Four 400 B SM type cell, identified as REFLEX project reference cell, were delivered to be tested in terms of both performance and durability. The most attention will be given to this type of cells with further modifications of all the layers and optimization of its microstructures and thicknesses.

2.2 Start up and reduction

During start up, the cell is fed with 20 Ndm^3/h argon flow to the fuel-electrode and 20 Ndm^3/h air flow to the oxygen-electrode. The cell is heated to 800 °C with ramp rate of 60 °C/h for the gold seal. At 800 °C, the NiO-YSZ electrode is reduced in a hydrogen and nitrogen mix (5% H2 / 95% N2; molar ratio) for 2 h followed by pure H2 for 1 h.

2.3 Performance evaluation

Electrochemical cell performance is evaluated performing three kinds of measurements:

- Electrochemical Impedance Spectroscopy at Open Circuit Voltage (OCV) and under current,
- Current-Voltage curve,

As cell performance depends on gas mix compositions and temperature, but also on operating mode (SOEC/SOFC) the tests plan consists in varying these parameters and recording actual performance of the cell.

Following Figure 2 details the flow chart of cell performances measurement process. As the three parameters mentioned above affect cell performance, the flow chart presents three levels nested loops:

- Temperature,
- Gas mix composition,
- Operating mode (SOEC/SOFC, notice that switch in operating mode is relevant only for gas mix composition CMG-3 and CMG-4 see Table 3).

In addition, two impedance spectra will be measured at +0.5 and -0.5 A/cm^2 in the pH_2/pH_2O 50/50 vs air gas composition inside loop 3 but occurs only once per temperature at CMG-3 gas composition.

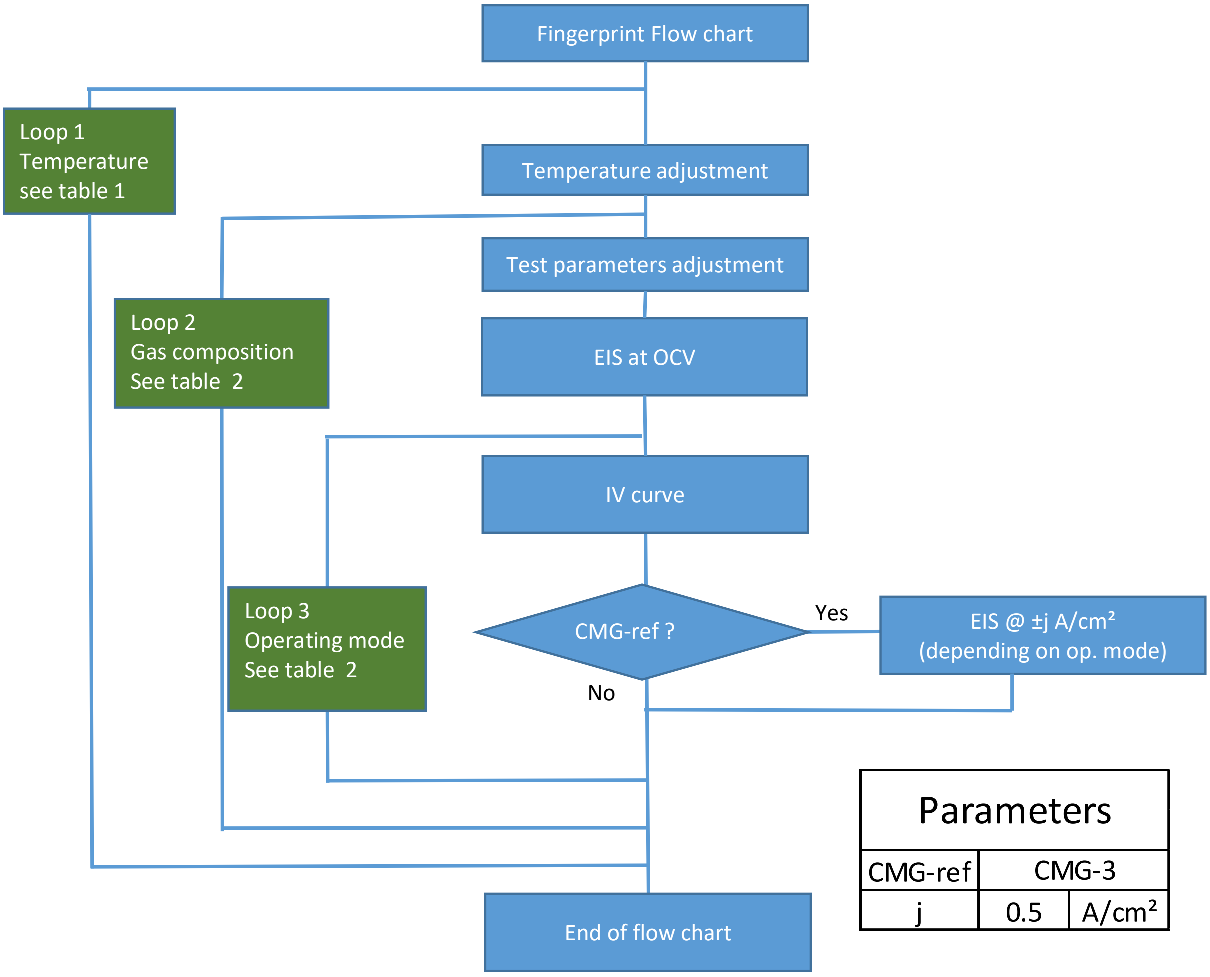


Figure 2: Performance characterization flow chart

Table 2 details tested temperature matrix. Notice that 700°C test will be repeated to check reproducibility of tests.

ID	Temperature levels °C
CT-1	750
CT-2	700
CT-3	650
CT-4	700
CT-5	800

Table 2: Cells testing temperature levels

Table 3 summarizes tests conditions and links each set of parameters (couple of feeding flows, composition of feeding gas mix, operating mode) to an identification number indicated in the first row.

ID	Flows		Composition					Mode	
			H2-side			O2-side			
	H2-side Ndm3/h	O2-side Ndm3/h	H2	H2O	CH4	N2	O2		
			%	%	%	%	%	SOFC	SOEC
CMG-1	25	100	96	4	0	80	20	x	
CMG-2			80	20				x	
CMG-3			50	50				x	x
CMG-4						0	100	x	x
CMG-5			80	20				x	
CMG-6			96	4				x	
CMG-7			96	4		80	20	x	
CMG-8			10	90					x
CMG-9			100	0				x	
CMG-10			0	66.7	33.3			x	

Table 3: Cell test conditions

Notice that:

- CMG-7 is identical to CMG-1, in order to check the stability of the testing process.

2.4 Cell Durability

Cell durability and degradation will be quantified by mean of four kinds of test.

2.4.1 Long term Test #0: Base line comparison

The aim of this test is to check the consistency of operating modes and test facility by reproducing a test classically performed by cell supplier ELCOGEN to qualify cell production.
By such a test one could expect to identify misoperation or any default on testing bench before starting the specific part of the REFLEX test protocol.

This test will be performed only once at cell testing task starting using the following parameters reproducing ELCOGEN's protocol:

Operating Mode	Current density A/cm²	Mix gaz molar ratio				Temperature °C	Reactant utilization rate		Test duration h
		H2 side		O2 side			H2 side	O2 side	
		H2 %	N2 %	N2 %	O2 %		%	%	
SOFC	0.25	50	50	80	20	650	40	20	500

Table 4: Baseline test #0 parameters

2.4.2 Long term Test #1: Stationary durability test in rSOC mode at 700°C

The aim of this test is to quantify degradation trends for each operating mode on steady state operation before to start alternative operating.

This test will be performed using the following parameters (see Table 5).

Operating Mode	Current density A/cm²	Mix gaz molar ratio				Temperature °C	Reactant utilization rate		Test segment duration h
		H2 side		O2 side			H2 side %	O2 side %	
		H2 %	H2O %	N2 %	O2 %				
SOFC	TBD after IV curves	96	4	80	20	700	85	20	250
SOEC		10	90				85	NA	250

Table 5: Cell long term test #1 parameters

Notice that during long term tests EIS under current will be performed periodically to check degradation and identify the nature of degradation.

2.4.3 Long term test #2: Long term reversible operation

The aim of the test is to operate as close as possible to the targets specified for in-field operations. Following Table 6 presents targeted test conditions, conform to Reflex project expectations. In case of lower performance measured performing IV curves, the current density and voltage could be adjusted.

Operating Mode	Current density A/cm²	Voltage V	Mix gaz molar ratio				Temperature °C	Reactant utilization rate		Operating time per day h	Expected degradation rate %/kh
			H2 side		O2 side			H2 side %	O2 side %		
			H2 %	H2O %	N2 %	O2 %					
SOFC	0.6	≥0.8	96	4	80	20	700	85	20	16	1
SOEC	-1.2	≤1.3	10	90				85	NA	8	

Table 6: Set of conditions for long term test in rSOC mode

For SOFC/SOEC mode transitions current will be decreased at ± 0.4 A/cm²/mn rate. At zero current OCV will be checked by a minimal stop (<1mn) systematically and every 2 days one impedance spectrum will be measured. This test will be ended after 1000h or when voltage in SOEC mode reaches 1.6V.

2.4.4 Long term test #3: Significant degradation limit evaluation

The aim of this test is to quantify threshold current density involving, in SOEC mode, degradation rate higher than expected for final product.

This test will be performed in alternative mode (SOFC/SOEC) by periods of 250h during which 16h/8h cycling is performed between SOFC mode and SOEC mode.

SOFC operation parameters stay the same for the total duration of the test.

SOEC current density is decreased by steps of - 0.3 A/cm² at the end of each 250 h great period, from -0.6 A/cm² until voltage reaches 1.6V threshold.

Operating Mode	Current density A/cm²	Mix gaz molar ratio				Temperature °C	Reactant utilization rate		Test segment	
		H2 side		O2 side			H2 side %	O2 side %	Operating time per day h	@ fixed current density h
		H2 %	H2O %	N2 %	O2 %					
SOFC	0,6	96	4	80	20	700	85	20	16	1000
SOEC	Initially -0.6 decreased by -0.3 step	10	90				85	NA	8	

The plot Figure 3 illustrates stepping up the SOEC-mode current density e.g. every 250 h.

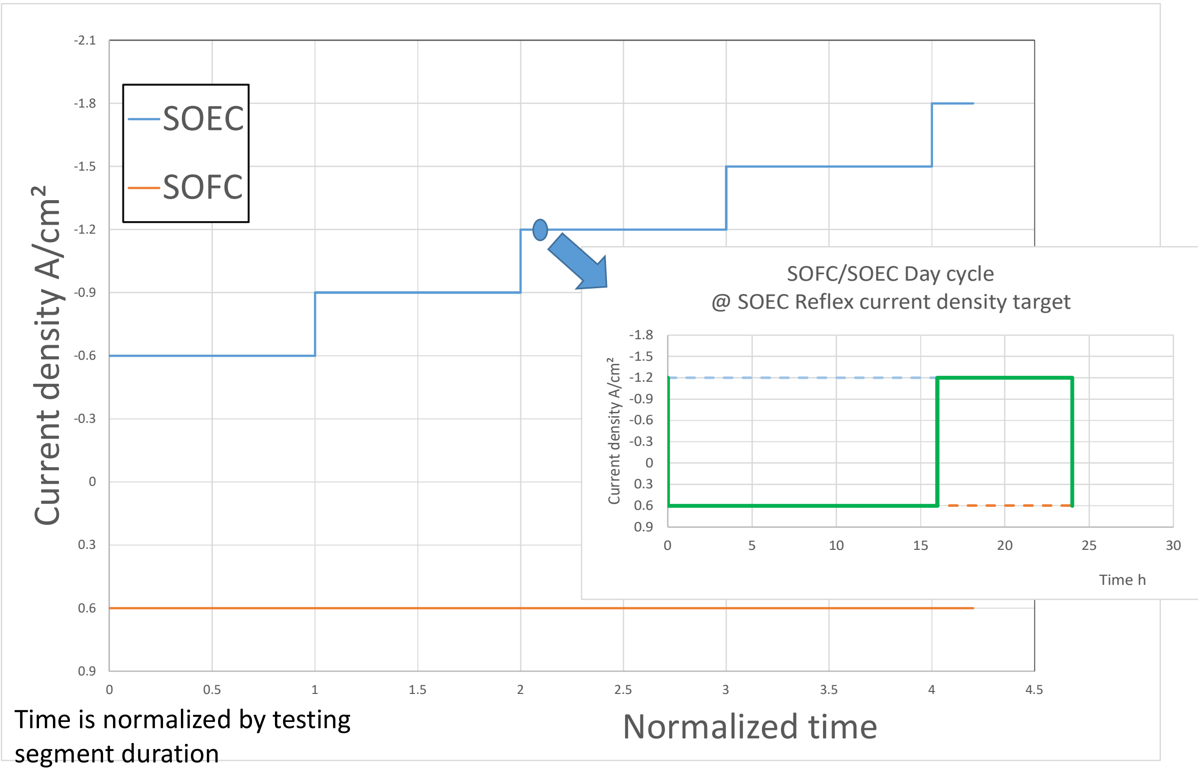


Figure 3: Current density Vs time during significant degradation evaluation test time

2.5 Stand by and safety mode

When the safety-system of the test-rig triggers – for example due to H_2 or CO sensors detecting an unsafe level due to gas leakage, or loss of gas supply, or users opening the door of the rig – all fuel-side gas flows are automatically stopped and the 20 Ndm^3/h 5% H2 + 95% N2 mixture mentioned earlier flows to the fuel electrode to protect the nickel from re-oxidizing.

2.6 Shut down

At the end of the test, the fuel-side gas flows is set to the 20 Ndm^3/h 5% H_2 + 95% N_2 mixture and the oxygen-side flow is set to 20 Ndm^3/h air, and the cell is cooled down to ambient temperature at 60 °C/h.

2.7 Test house

Following figures present cell testing experimental set up at DTU.

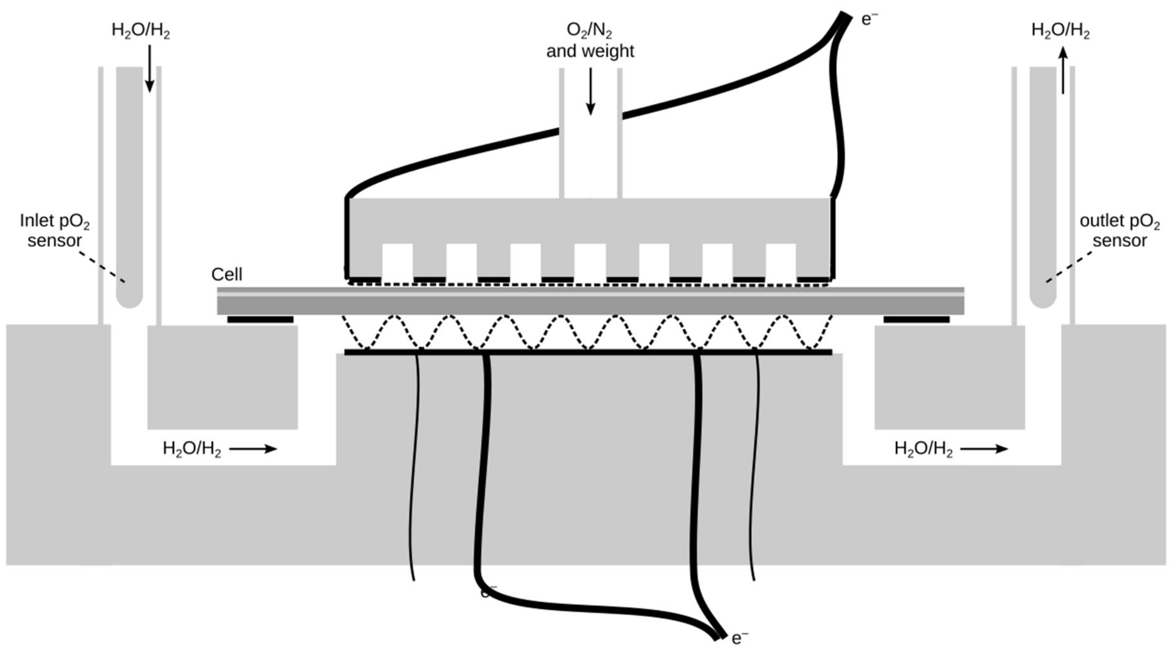


Figure 4: Sectional drawing of experimental set up

Figure 4 is a sectional drawing of the set up showing gas mix distribution for both sides of the cell, electrical connection, sealing location, electrical probes, etc.
Notice that in operation number of voltage probes is higher than represented here.

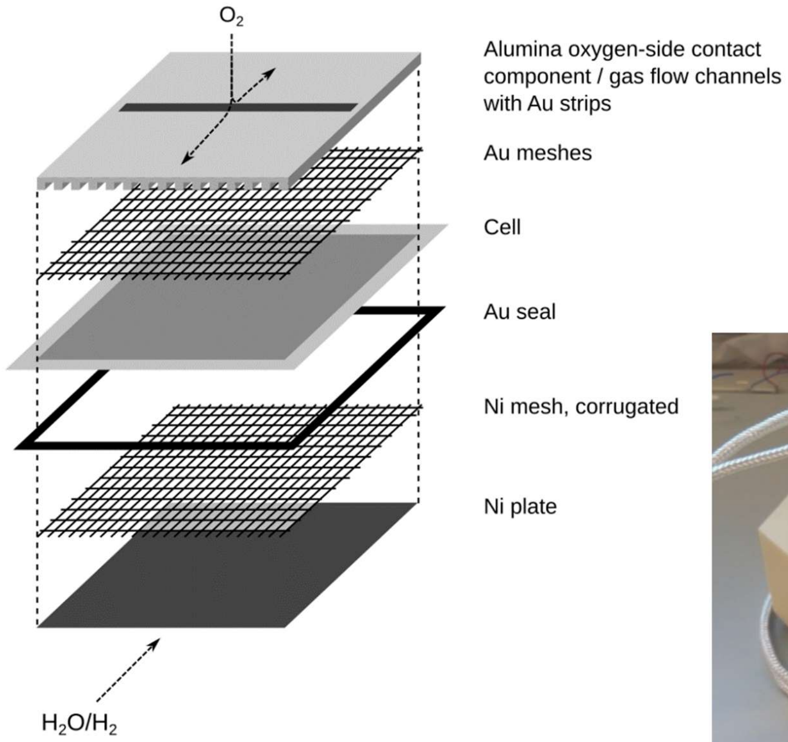


Figure 5: Exploded view of cell testing pile

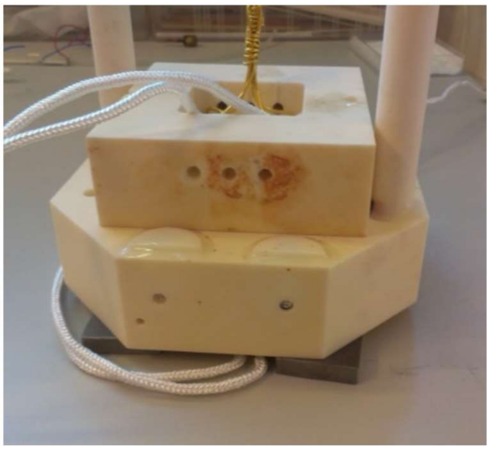


Figure 6: Photography of cell test-house

Figure 5 details parts added to cells for current distribution and collection.
On the fuel side, nickel plate and corrugated nickel mesh distribute/collect electrons. On the oxygen side electrons distribution/collection is performed by mean of a gold mesh inserted between oxygen distribution plate and cell. Gas distribution channels are machined on oxygen distribution plate, made

of alumina. Resulting alumina walls bottom faces are covered by gold strip insuring electrical continuity.

3. Stack testing protocol

Stack testing task can be represented by a flow chart including six steps as shown in Figure 7.

During first step stacks are heated up, reduced and conditioned. It will be done at CEA. For partners testing stacks, they will only have to heat it up in defined conditions by CEA. Then intrinsic electrochemical performances are measured. A first long term test gives trends on degradation under extra low switching mode frequency.
Performance characterization is repeated to quantify the impact of the first long term testing step. A second long term test is performed switching from SOFC mode to SOEC mode once a day. Operating period under each mode is defined to simulate in-field situation.

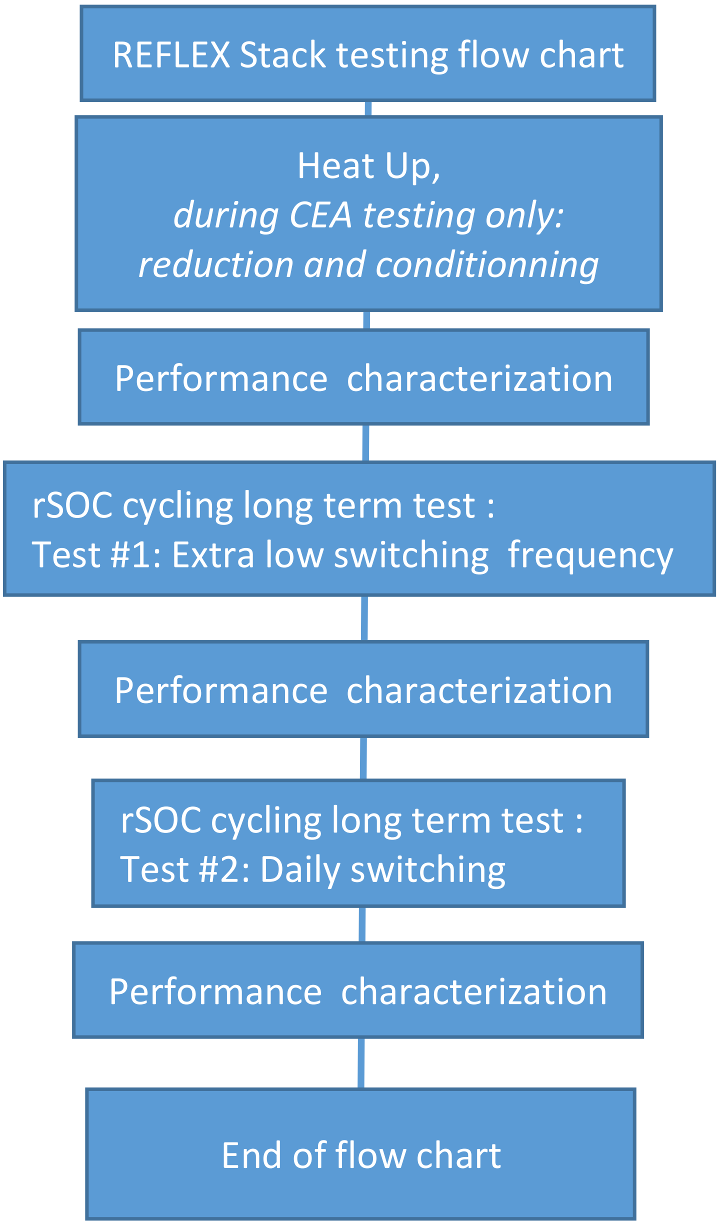


Figure 7: Stack testing flow chart

3.1 Stack Heat up

Stack heat up will be performed at temperature rate of 60 °C / h, mix gas flow is presented in Table 7.

Step ID	Temperature rate (°C/h)	Flow on H2 side (Ndm3/h/cm²)	Flow on O2 side	Composition on H2 side		Composition on O2 side
SC-1	60	0.18	similar	3%H2	97%N2	100%N2

Table 7: Set of conditions for stack heat up

3.2 Performance evaluation

Electrochemical stacks performance is evaluated performing two kinds of measurements:

- Current-Voltage curve (IV curves).
- Electrochemical Impedance Spectroscopy,

As stack performance depends on gas mix compositions and temperature, but also on operating mode (SOEC/SOFC) the tests plan consists in varying these parameters and recording actual performance of the cells into the stack.

Following Figure 8 details the flow chart of stack performances measurement process. As the three parameters above affect stack performance, the flow chart presents three levels nested loops:

- Temperature,
- Gas mix composition,
- Operating mode (SOEC/SOFC, notice that switch in operating mode is relevant only for gas mix composition SMG-4 see Table 9).

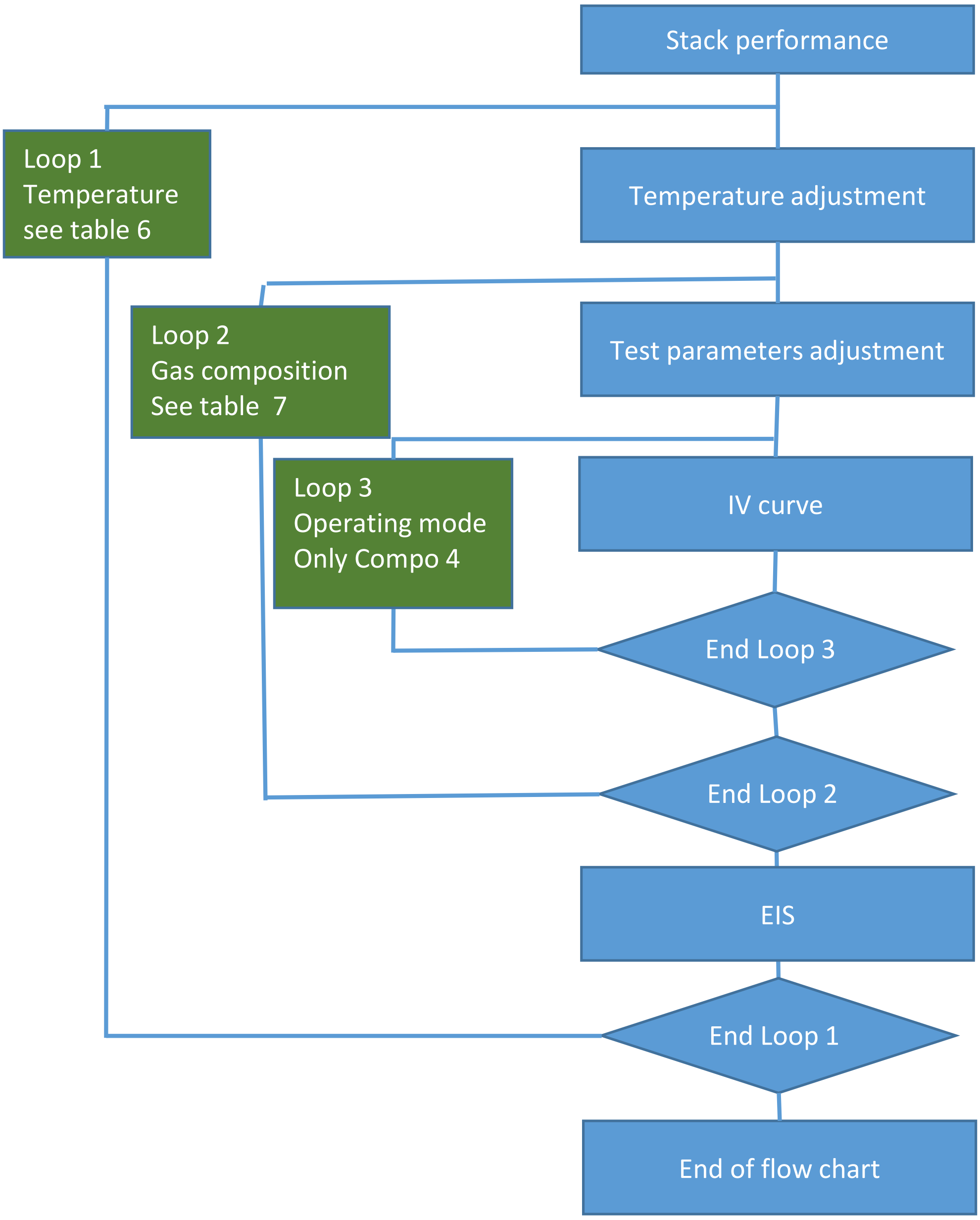


Figure 8: Performance characterization flow chart

Table 8 details tested temperature matrix.

ID	Temperature levels °C
ST-1	800
ST-2	750
ST-3	700

Table 8: Stacks testing temperature levels

Table 9 summarizes gas mix composition and flow rates conditions defined for IV curves and EIS. It links each set of parameters (couple of feeding flows, composition of feeding gas mix, operating mode) to an identification number indicated in the first row.

ID	Operating Mode		H2 Side Total flow rate Ncm3/min/cm²	O2 side Total flow rate Ncm3/min/cm²	Mix gaz molar ratio				
					H2 side			O2 side	
	SOFC	SOEC			H2 %	H2O %	N2 %	N2 %	O2 %
SMG-1		x	12	Adjusted to get controled differential pressure between chambers	10	90	0	80	20
SMG-2		x	6						
SMG-3		x	18						
SMG-4	x	x	12	14.3	50	50	0		
SMG-5	x				50	0	50		
SMG-6	x		3	7.8	100		0		

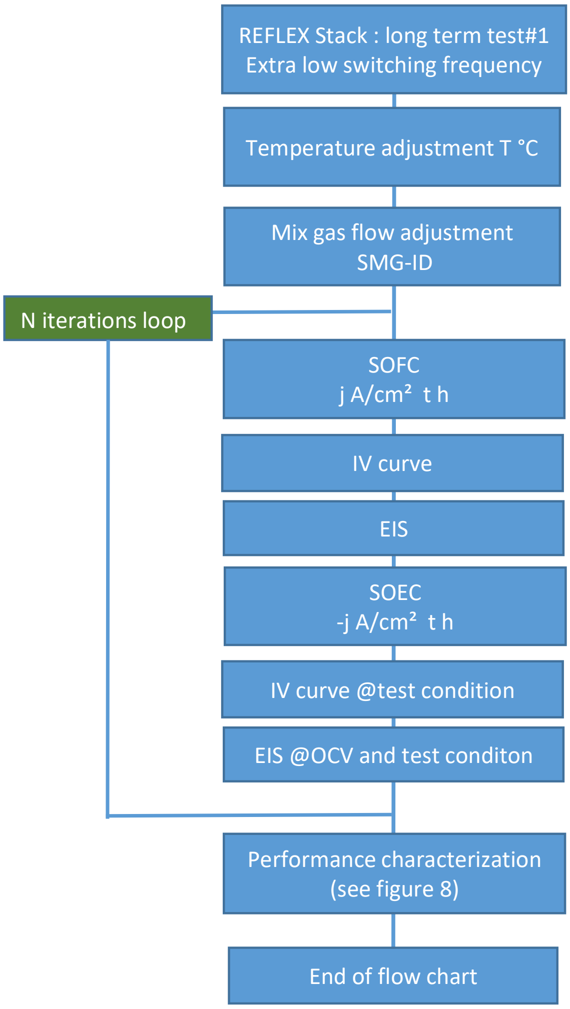
Table 9: Mix gas composition set for IV curves and EIS

3.3 Durability under rSOC cycling

Stack durability tests temperature level is consistent with Sylfen's energy hub temperature target of 700°C.

3.3.1 Extra low switching frequency

The aim of this test is to quantify stack degradation after long period (≈100 h) switching between SOEC and SOFC mode decoupling current and gas composition effects.
Total duration of the test is about 800 h, four periods for each mode.
Following Figure 9 presents the associated flow chart.



Parameters		
T	700	°C
SMG-ID	SMG-4	
N	4	
j	0.5	A/cm²
t	100	h

Figure 9: Extra low frequency long term stack test flow chart

Gas mix flow/compositiono is the same for SOFC and SOEC periods, it corresponds to gas mix SMG-4 of Table 9.
Targeted absolute value of current density, 0.5 A/cm², is the same for each mode.

3.3.2 Daily switching

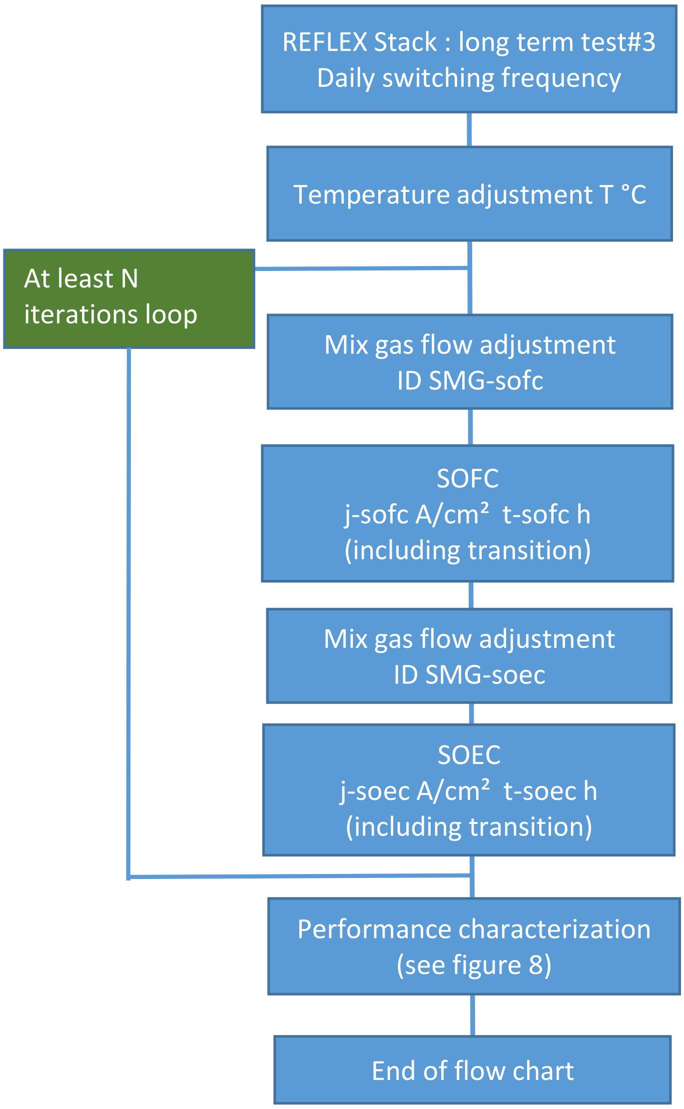
Smart energy hub main function is to store renewable electricity excess production by electrolysis and restore it, when needed, by fuel cell electrical production. It is so meaningful to qualify how switching from one operating mode to the other frequently impacts stack durability.
Total duration targeted for the test is at least of 480 h.

Targeted day cycle is the following, but could be adjusted depending actual stack performance at the beginning of the test:

- SOFC mode :
    - Temperature : 700°C,
    - Mix gas flow : SMG-6 Table 9,
    - Current : 0.6 A/cm²,
    - Duration : 16 h.

- SOEC mode :
    - Temperature : 700°C,
    - Mix gas flow : SMG- 1 Table 9,
    - Current : -1.2 A/cm²,
    - Duration : 8 h.

Figure 10 presents the associated flow chart.



Parameters		
T	700	°C
SMG-sofc	SMG-6	-
SMG-soec	SMG-1	-
N	20	-
j-sofc	0.6	A/cm²
j-soec	-1.2	A/cm²
t-sofc	16	h
t-soec	8	h

Figure 10: Daily switching test flow chart

3.4 Standby and safety mode

In case of standby or any problem, mix gas flow conditions correspond to SMG-2 of Table 9.

3.5 Shut down

Stack cooling will be performed at 1°C/mn rate, hydrogen chamber fed by hydrogen 3% nitrogen 97% mix, oxygen chamber fed with nitrogen. Flow rates are adjusted to insure a maximum differential pressure between chambers of 5 mbar.