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Gas-tightness studies at high temperature: application to SOE

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Abstract

When designing industrial Solid Oxide Electrolysis systems, the gas-tightness of the inner parts and auxiliaries is a technical subject requiring dedicated attention. The stacks and its interfaces located in the hottest location inside the module have to be gas-tight in a very harsh environment imposing stringent limits and constraints on the technical sealing solutions that can be implemented. These constraints become even more challenging when considering a stack architecture with two chambers fed with pressure levels significantly above the atmospheric pressure (i.e. 100 to 300mBarg).

This paper addresses the general topic of the gas-tightness requirements and their impacts on systems and stacks design and operation. Defining the leak-rate requirements with the specificities of the technology is discussed. With far-reaching impacts at all levels, leak-rate requirements are indeed parameters that have to be chosen appropriately. All in all, most of the leakage issues can be overcome by proper technical and pragmatic approaches. Through several examples - room temperature manufacturing acceptance tests, high temperature qualification on full-size stacks in steady operation - results and practical methodologies that can be implemented to evaluate leak-rates are described and discussed.

INTRODUCTION

When performing a functional analysis of Solid Oxide Electrolysis (SOE) system, on of the primary function of the equipment ended up being the processing of hot gases aiming at the production of hydrogen. A function that quickly derived to a secondary function linked to its ability to ensure gas-tightness. From the compilation of the constraints linked to the gas-tightness requirements of the sub-parts of the system, it quickly appears that this technical function is a rather challenging objective to achieve. Focusing on the foremost-constrained component of SOE system, namely the stack, the technical constraints applied on the sealed interfaces combined all the features (Figure 1) one does not like to deal with when designing a gas-tight component. The gases processed, that includes hydrogen known for its high diffusivity, the high operational temperatures and the possibly complex geometries of the sealed interfaces are by themselves complex to solve. Add to this the electrical requirements (with sealed interfaces that have to provide electric insulation between layers) and the low levels of compression force available to ensure the compression between your interfaces to limit the constraints at high temperature. It all adds up to end with a very narrow list of technical options. Indeed, either for sealing solutions based on compressive, compliant or solid seals [1], the list of materials providing electrical properties, thermal and mechanical resilience at high temperature, together with sealing properties and thermal expansion behaviour compatible with the SOE stacks technical constraints ended to be very restricted. Additional manufacturing and techno-economical aspects can also be added to the list

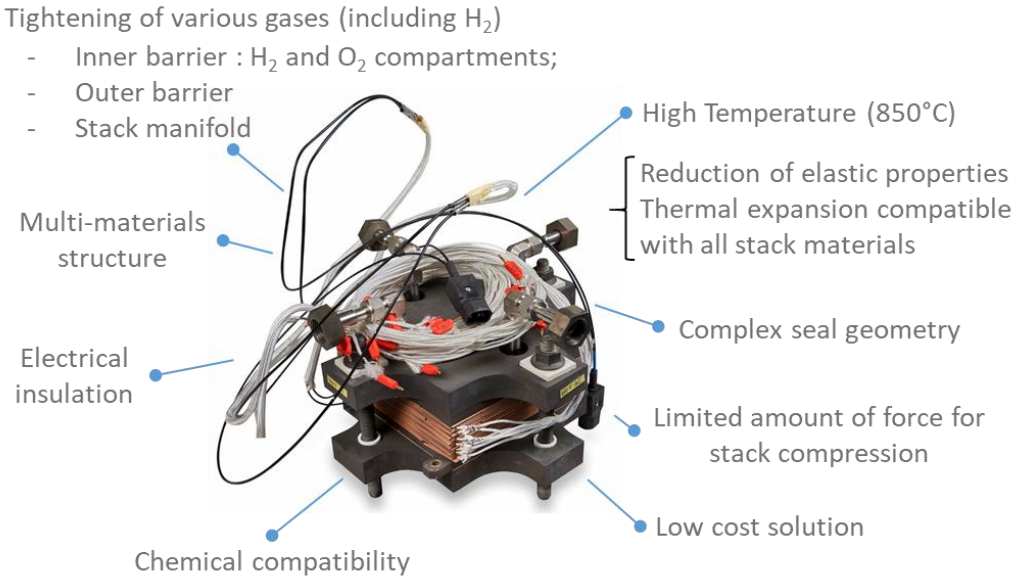


Figure 1 – Technical constraints associated with SOFC&SOEC stacks leak tightness.

Despite these tedious constraints, several solutions have been developed over the years. Among these solutions, rigid seals (or cement) made of glass or ceramic/vitro-ceramic are widely used. When properly formed, this type of seals that can allows the formation gas-tight barriers with very low leak-rates [2] has been chosen as the reference solution in our components.

1. Leak-rate criteria

When implemented on SOE system, the leak-rates commonly measured on stacks made of tens of Single Repeatable Unit (SRU) are several decades above the values measured on

samples of small-scale components. The leaks observed on stack can be in most of the case considered as leak in the viscous flow regime, far from the molecular flow regime than can be obtained on test small-scale samples. Indeed, inside a stack the global leak-rate no matter the solution implemented is always the results of the sum of the defects within the sealed interfaces leading to the formation open leak-paths. The complex geometry of the sealing barriers with lengths that can exceed two meters per SRU (in our current stack design) and hundreds of meters on large stack structure combined with the constrains mentioned above contribute to the degradation of the gas-tightness. Therefore, the intrinsic gas-tightness performance assessment on samples of a given solution can hardly be considered to define a leak-rate requirement, taking the risk to impose unachievable technical requirements on the stack. The definitions of leak-rate requirements, global or applied on a specific system component, have to be addressed with caution. The leak-rate requirement can complicate not only the design of the stack, but also the design of the hotbox and of the whole system. For example, the easiest way to reduce the leak-rate is to maintain the pressure inside the gas chambers as low as possible, a target achievable with well-designed SRU/module and system architectures featuring low-pressure drop but with significant operational impacts. The quadratic dependence of the mass leak-rate with pressure explained why most of the high temperature SOE systems are today operating in “quasi-atmospheric” conditions. When considering stack architecture with two chambers fed with pressure levels significantly above the atmospheric pressure (i.e. 100 to 300mBarg), a pragmatic approach is required to define a reasonable leak-rate criteria.

When considering a stack on its own, outer and inner leaks have to be considered separately. The outer leak, resulting from the presence of a network of leak-paths on the stack outer structure and interfaces (manifold plate), is created by the pressure gradient between the gases inside the stack and the atmospheric pressure. As quoted above, this leak is commonly rather high and can be considered a viscous flow. The inner leak between the gases chambers inside the stack mostly though the cell is by nature very different with leak-rates levels (strongly function of the cell technology and structure) orders of magnitude below the outer-leak. The leak-rate of the glass-ceramic seal ensuring the gas chambers tightness located between the cell and the interconnector plate is lower than the leak due to the permeability/porosity of the cell. The criteria and methods that can be used to measure or at least perform acceptance tests on inner/outer sealed interfaces are quite different.
The more common methods for leak detection at high temperature implemented on EHT are based on electrical measurements. The Open Circuit Voltage (OCV) provide interesting information regarding the stack tightness reflecting theO2 concentration inside the H2 compartment. The measurement can be made with gas-flow (not discussed here) or in steady conditions [3] [4].The Electrochemical Tightness Test (ETT) protocol is the following: starting in a steady initial state with dry H_2 and air, the ETT consists in switching off the inlet gases and recording the rate of the OCV drop over time. The gas outlets can be either closed or kept open. A quick decrease can be associated to a leak between the inner chambers and a slow decrease indicates limited gases exchanges. Based on the slope of the OCV decrease leak-criteria can be defined and used as acceptance criteria. This method is rather efficient to detect defects on the inner sealed interfaces (cells or seals). The ETT has a sensitivity relying on the number of the voltage measurements implemented on the stack structure. If only few SRU are instrumented, the mean voltages measured will only provide a rough estimate and localisation of the defect. The main drawback of this method is the potential risk of damaging the stack if the test is not performed with caution. Indeed, in case of tightness loss between the chambers a significant O_2 inlet without gas flow in the fuel chamber can lead at high temperature to severe and irreversible damages on the cell. A non-mastered ETT made to qualify minor defects (with little impact on the stack operation)

can lead to the ruin of the stack if the test is not stopped in due time. This test is particularly risky for cathode-supported cells, since the volume increase of the cermet induce by an air leak is far greater than the standard electrolytes thickness.

Concerning the outer-leaks, it is important to note that the leak-rate value measured by most methods is often the sum of the leaks on the inner and outer sealed interfaces of the two gases chambers. The cell inside the stack isolates the two gases chambers and presents a large exchange area, therefore any improvement on the outer sealed interfaces have to be compared to the inner leak. Whereas the inner leaks due to important defect such as cell cracks have most of the time dire consequences on the stack operation, outer leaks are less crucial especially on the O_2 side. On the H_2 side, the main risk that can be associated to a defect/crack on the outer sealed interfaces is the formation of flow of H_2 generating a hot spot able to degrade the stack outer or inner structure. Such phenomenon can occur when the defect is able to form a localized stream of gas generating damages than can propagate and lead to a destruction of the stack

If the choice of the inner leak-rate criteria is defined by the cell technology, different technical approaches can be considered to define a proper outer leak-rate criterion. Safety related issues are the first that come to mind. The hotboxes can be monitored by O_2, H_2 or CO gas sensors allowing the detection of abnormal gas composition generated by a gas leakage. The sensitivity of these sensors are rather low and must be correlated with the flow-rate of the gas venting the hotbox. However, leak-rate criteria based on ATEX considerations, compliant with the sensitivity threshold of the detection system integrated in the hotbox, do not appear to be an interesting approach when defining an acceptance criteria for a stack. With a primary safety objective to prevent severe fire-damages inside the hotbox, the leak-rate levels that can be detected by these types of systems are indeed commonly above values allowing a proper operation of the stack. Another approach can be economic, related to the acceptable amount of production losses. A stack with a gas-tightness on the H_2 side limiting the losses to 1% or less of the global production is generally considered as a good value in terms of standards, allowing a safe and steady operation of the module. This 1% is also coherent in regards of thermal considerations. The thermal impact of a 1% leak-rate on the H_2 flow-rate can be estimated. The Lower Heating Value (LHV) of hydrogen is 3.0 $kWh.Nm^{-3}$ = 5.10^{-5} $Wmin.NmL^{-1}$ [5]. Considering a standard operating point at 700°C with gas flow-rate of 10 $NmL.min^{-1}.cm^{-2}.cell^{-1}$, a leak-rate of 1% on a SRU with a $200cm^2$ cell can be associated to a heat exhaust of 0.1 $W.cell^{-1}$. On stack structures made of hundreds SRU, this value of tens of watts compared to the few kW of the hotbox heating power remains modest. No matter the criterion chosen, the question of imposing a leak-rate criterion different on the O_2 and H_2 side on a SOE system can be discussed, acceptance value higher on O_2 side than the one imposed on the H_2 side can be chosen without impact on the operation of the system. The gas-tightness on the O_2 chamber has to be good enough to provide a counter pressure compatible with the H_2 chamber pressure for a given inlet flow-rate. This 1% criterion also makes sense in regards of the method that can be implemented to measure the stack gas-tightness. Indeed, once the leak-rate criterion has been chosen, the measurement of the stack gas-tightness is the second question to be addressed. The most common way to monitor the leak-rate in real-time at high temperature during production in a module is to compare at the given operating point (voltage/current) the inlet and outlet flow-rates. The inlet/outlet difference that can be referred as Collection Rate (CR) provides a rough estimate of the gas losses. Considering the accuracies of the mass flowmeters and the uncertainties on the gases stoichiometry, the sensitivity threshold of this method is in the range of 2-5% of the gases flow-rate. Even if the sensitivity threshold of the measurement method used in operation is above the 1% leak-rate criterion, a choice of a

value close and below levels allowing the safe operation of the stack is coherent. Experience shows that stacks with gases losses exceeding 8% of the total flow-rate can be operated without major safety issues but with some impact on their performances. The CR method is very convenient and easy to implement on stack but rely on well-calibrated mass-flowrate.
Two others classical types of methods can be implemented to measure the outer leaks: the Pressure Drop/Raise Measurements (PDM/PRM) and mass-flow rate measurements coupled with pressure feedback control. Both methods cannot be implemented during system operation due to the tests requirements. For the PDM/PRM, the chambers have to be filled up to a chosen pressure and then isolated therefore the production has to be stopped to proceed with the test. It is handy to perform these tests with the same gas (pure N_2 or Ar) on the two chambers at pressure level close to operating conditions. Leak-rates in the range of 10^{-2} to 10^{-5} $Pa.m^3.s^{-1}$ can be measured with this type of method [6]. The lower range of this method corresponds to the acceptable time allowing a proper measurement of the pressure drop. The upper range is based on the accuracy of the pressure transmitter and tests conditions. The method requires a steady temperature and a fine estimate of the chamber and associated gas line volumes. For a given leak, the larger the volume, the longer is the integration time required to perform the measurement. Like the ETT method, significant O2 leakage (inner or outer) inside the H2 chamber without can lead to severe damages on the cell.

At high temperature on a system in operation, with several stacks connected to the same gas lines, the implementation of this method can become very complex and most of the time impossible to implement. With leak-rates in the range of few percent of the flow-rate, the methods based on mass-flow measurements combined with feedback-controlled pressurization of the chambers are simpler to implement. Like the pressure drop method, the gas outlets have to be closed and the H_2 production stopped. The measurement range of this method is wider with a lower sensitivity (considering a convenient operation on stack and module) in the range of 1-5 $NmL.min^{-1}$. The measurement of the pressure together with the flowrate allows a direct leak-rate estimation either with an imposed pressure or with an imposed flowrate. Both methods provide means to monitor of the stacks tightness inside the hotbox at high temperature and compatible with the 1% criterion. These methods can also be implemented at Room Temperature (RT) to perform Fabrication Acceptance Test (FAT). Low-pressure cold measurements can be used to estimate high temperature leak-rate for a given operating point.

2. Implementation of leak-rate measurement on stack: practical examples

To support the technical developments of SOE technology at CEA LITEN, test-benches and protocols dedicated to sealing studies have been developed. In the following, test results on full size stacks are presented. In our design, the SRU is composed of thin interconnectors using 0.2mm ferritic stainless steel sheets. It comprises electrode-supported cells of 100 or $200cm^2$ in active area. A nickel-mesh and a LSM contact element are set in the H_2 and O_2 compartments respectively. The sealing interfaces between SRU are made by sandwiches mixing vermiculite plates and a commercial glass-ceramic. The sealing of the inner gases chambers is ensured by a glass-ceramic paste deposited on the periphery of the SOC cell, directly on the dense electrolyte. The specific (and yet rather complex) design of the sealed arrangements allow standard stack operation at pressure levels exceeding 300mbar. More details on the stack architecture and inner components can be found in [7] [8] [9].

2.1 - Fabrication Acceptance Test: comparison between RT and high temperature leak-rate measurements

A series of 16 stacks (25 SRU with 100cm^2 cells) were assembled in our workshop. Getting use to qualify stack prototypes made in few copies that can hardly be compared one to the other, we took benefits of this large series of identical stacks to validate FAT based on RT mass-flow-rate measurements at low pressure. Assuming a viscous regime for the stack leak and a minor impact of the cooling on the stack tightness (hypothesis acceptable for FAT made on brand news stacks), thanks to proper correlations, the values measured at RT can provide estimation of leak at high temperature for any given operating point. At the end of their conditioning phase, each stack undergoes a series of electrochemical tests and CR were measured at different operating points. Calculated values based on RT measurements and the leak-rates measured at high temperature offer two sets of data that can be compared to assess the method.

To perform the FAT, the O_2/H_2 inlets and outlets of the stack are equipped with connections with valves allowing the closing/opening of the circuits (Figure 2). One of the gas chamber is pressurized to a selected set point with an auto-regulated mass-flowmeter and the other chamber is maintained at P_{atm} (with inlet/outlet opened or closed). Once the pressure set point is reached, the flow-rate needed to maintain the pressure provides a direct measurement of the leak-rate (Figure 2). If the same flow-rate is measured with the non-pressurized chamber open or closed, inner leak-rate can be considered negligible. Figure 2 illustrates the protocol. In this example, the H_2 compartment is tested at 15 and 30 mbars with the O_2 side open then closed. If no significant leaks are measured on the H_2 side, the leaks on the O_2 side are significantly higher.

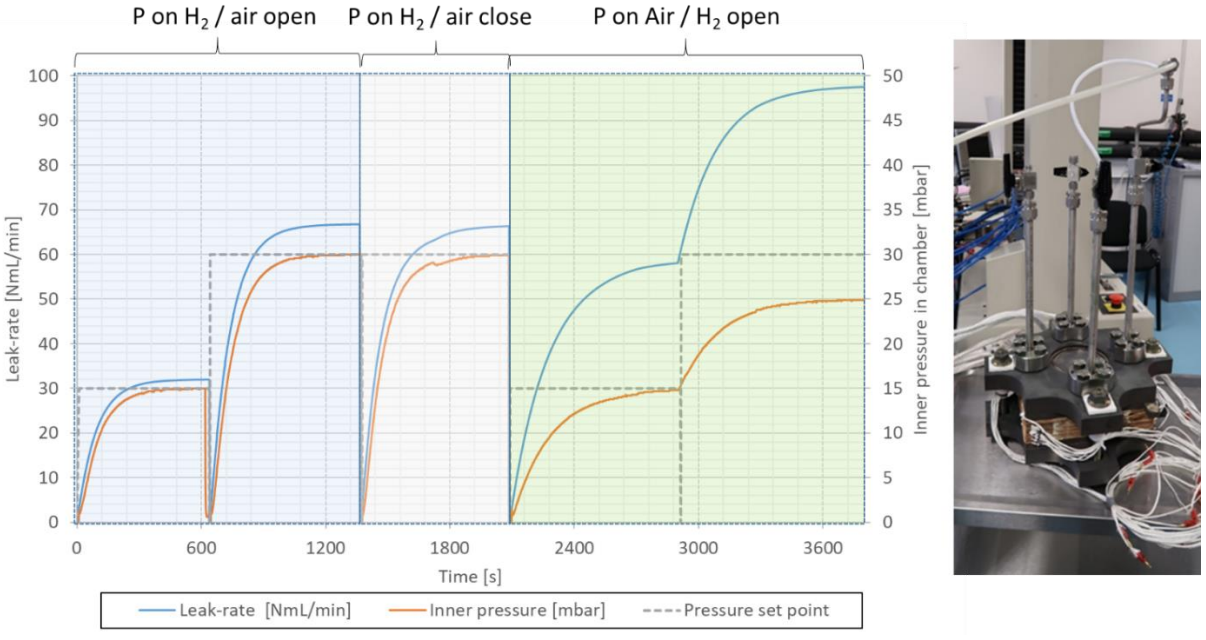
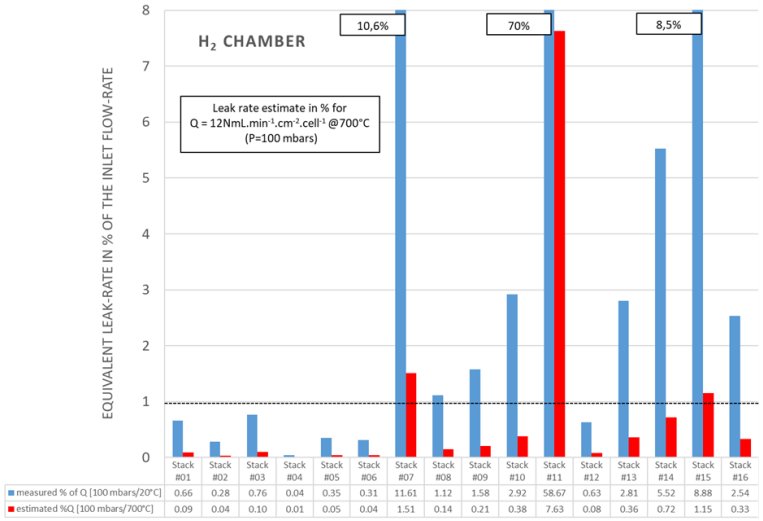


Figure 2 – Mass-flow rate measurements at RT on O_2 and H_2 sides on a 25x100cm^2 stack.

From the RT measurements, estimates of high temperature leak-rates can be made taking into account the impact of the temperature and gas composition on the leak-regime. These values can be compared to measurements of the recovery rate made at high temperature (Figure 3). The comparison between the estimation of leak-rates at high temperature (700°C/100mbars) made from the RT measurements and the CR are coherent. Considering

the accuracy of 2-3% of the recovery rate measurement and the hypothesis made for the calculation, the estimated values are in an acceptable range. Concerning the worst stack (#11), its low performances imposed a different operating point with a flow-rate of 8.7 $NmL.min^{-1}.cm^{-2}.cell^{-1}$. Based on this method, if the criteria of 1% of leakage is chosen for electrolysis operation, two stacks (#7 & 11) can be discarded for a future use inside a SOE module.



(a) Measurements of equivalent leak-rate at RT/100mbars and estimated values at 700°C

Réf. Stack	Collection rate on H_2 chamber Operating point : Q = 7,13 $NmL^{-1}.min^{-1}.cm^{-2}.cell^{-1}$ @ T=700°C P ≃ 100mbars
STACK #01	100%
STACK #02	100%
STACK #03	100%
STACK #04	100%
STACK #05	100%
STACK #06	100%
STACK #07	95%
STACK #08	100%
STACK #09	100%
STACK #10	100%
STACK #11(*)	88%
STACK #12	100%
STACK #13	100%
STACK #14	100%
STACK #15	97%
STACK #16	98%

(*) Q = 8.7 $NmL^{-1}.min^{-1}.cm^{-2}.cell^{-1}$

(b) Recovery rates measured at 700°C on H_2 side

Figure 3 – Comparison between measured leak-rates at RT, high temperature calculated values and recovery rates on 16 identical stacks.

2.2 - High pressure tests on stack under operating conditions

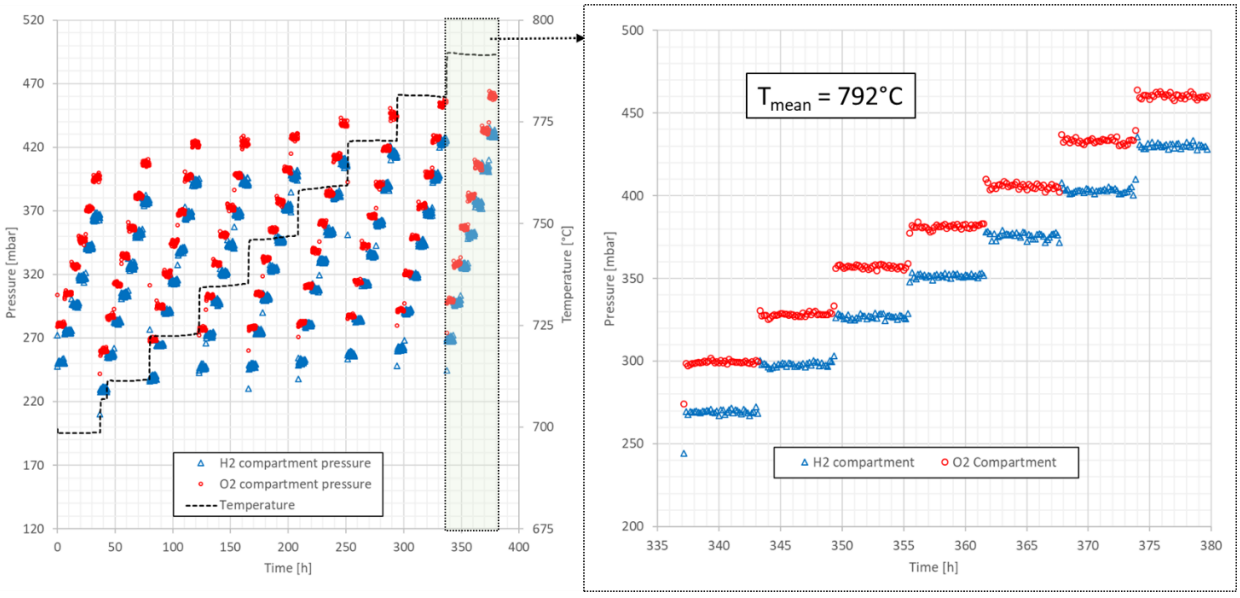


Figure 4 – Pressure resistance test on stack 25x100cm^2 between 700 and 800°C.

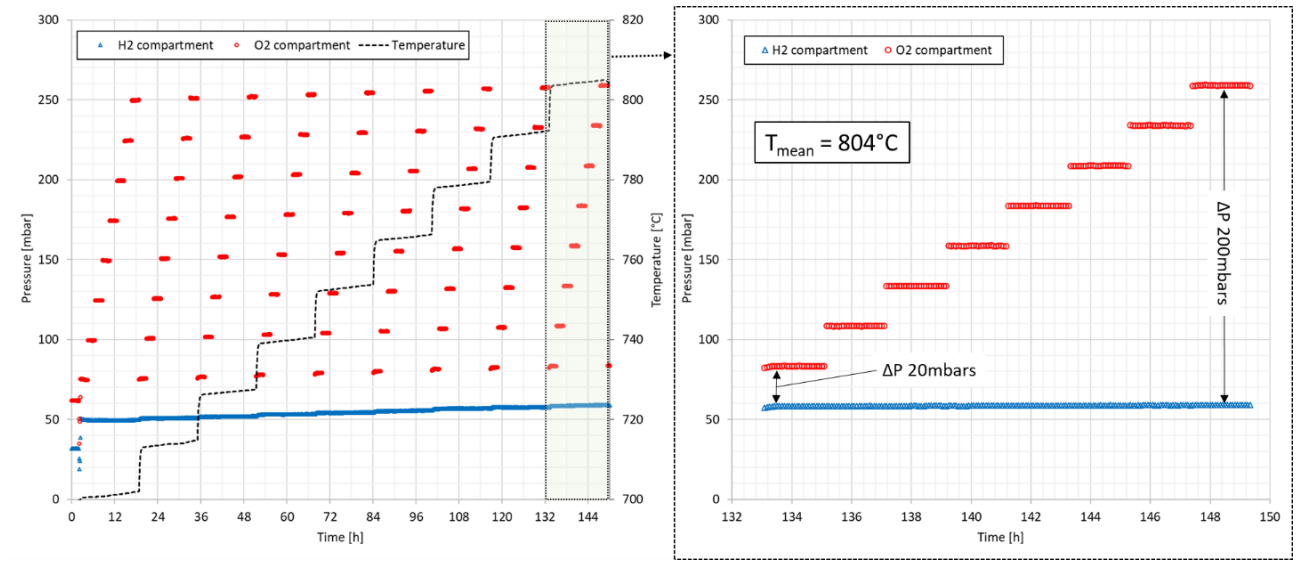


Figure 5 – Pressure resistance test of the inner sealed interfaces on stack 25x100cm^2 between 700 and 800°C.

If the qualification of a given sealing solution starts with tests at the sample scale, its integration within a stack requires full-scale tests in demanding conditions. Among the possible tests, pressure resilience tests [10] at levels far above the operating conditions provide an efficient and simple manner to qualify a technical option. Once the tests on small mock-ups are achieved, in order to qualify the pressure resilience of the outer sealed interfaces of the stack in more representative conditions, tests on a stack 25x100cm^2 (identical to the stack described above) were performed between 700 and 800°C (Figure 4). On each temperature steps (every 12.5°C), the inlet flow-rates of the two chambers were increased and adjusted to maintain a constant gradient between the H_2 and O_2 compartments and to raise step by step the stack inner pressure. In the meantime, the compression force applied on the stack was adjusted to maintain a steady pressure contact on the cell. The pressure levels were maintained during 5 hours on each steps, the leak-tightness and the stack performance were assessed by measuring the H_2 production (around 30 g/h) and the recovery rate (99-100%). The stack passed the test successfully with a maximal inner pressure of 440/460 mbars on H_2/O_2 compartment at 800°C. A second series of tests was then performed over identical temperature steps applying increasing levels of pressure gradient between the gases chambers (Figure 5). With the constant pressure inside the H_2 chamber, the O_2 pressure was raised by increasing the inlet flow-rate step-by-step. The test demonstrates the ability of the inner sealed interfaces (the seal below the cell) to withstand pressure gradient up 200 mbar at 800°C during two hours. Regarding the standard operating conditions, with a gradient in the range of 30 mbars, such tests demonstrate the pertinence of the technical solution implemented and the available margins.

2.3 - Volumetric leak-rate measurement on full-scale stack prototype

Dedicated leak-rate measurements were conducted on a 3x200cm^2 stack prototype to validate the integration our latest configuration of outer sealed interfaces (Figure 6). Thanks to very low leak-rates measured on the outer sealed interfaces, estimation of the inner leaks due to the gases exchanges through the cell inside the gases chambers was made possible.

After the conditioning of the stack followed by a cooling down and a series of thermal cycles, the stack was re-heated and using PRM method (with pressure gradient of 100 mbars) the leak-rates of the H_2, O_2 and of the two chambers combined were measured under N_2. The differences between of the algebraic sum of the measurements made on O_2/H_2 and on the measurement made on the O_2 and H_2 connected (therefore at the same pressure) provides a way to estimate the leak on the common inner barriers of the chambers mainly composed of the cells and its peripheral seal. The measurements made at different temperatures show that the leak between the chambers is not negligible because of the large exchange area offered by the 200cm^2 porous cell. The value derived from the measurement can be compared to the manufacturing cell leak-rate acceptance level of 1.2 10^{-5} Pa.m^3.s^{-1}.cm^{-2} (discontinuous dotted line on Figure 6) for non-reduced cell at RT. More than very low leak-rates of the outer sealed interfaces that have been achieved thanks to a proper design and a mastered manufacturing, these results point out that the inner-leaks have to be considered in global leak-rate measurement.

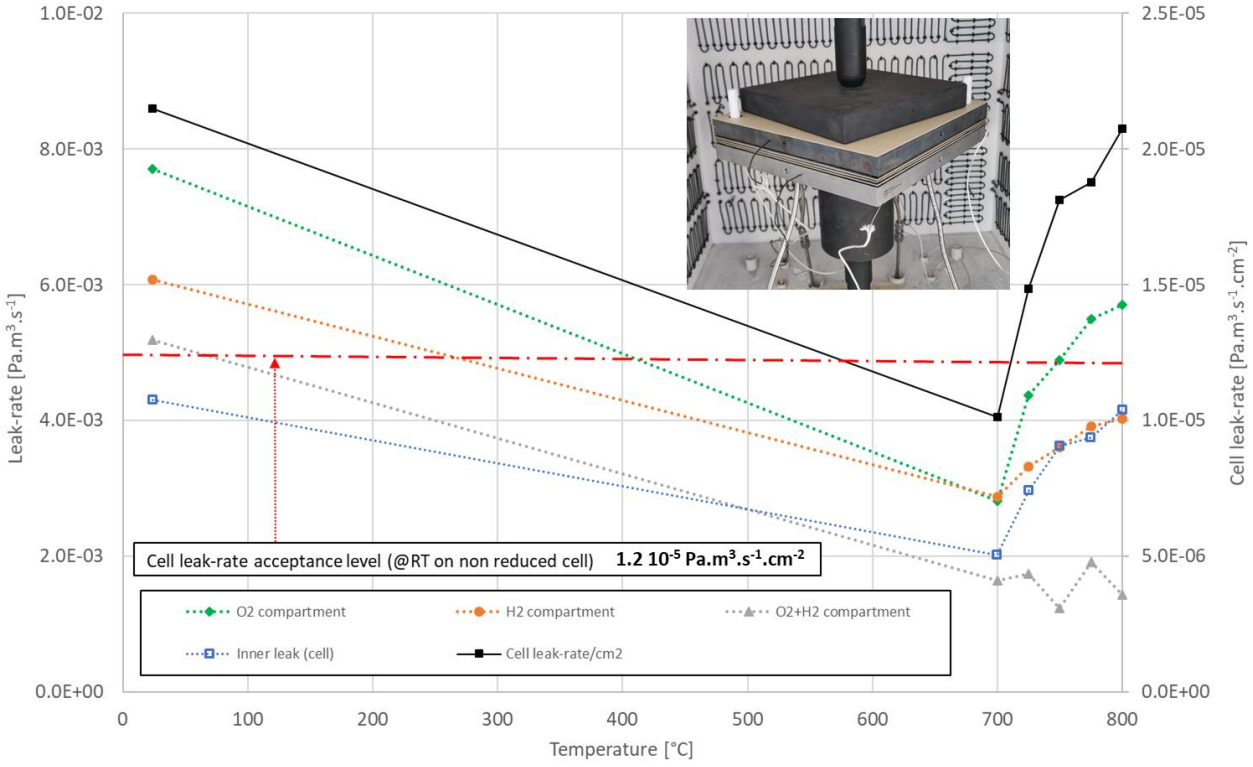


Figure 6 – Volumetric leak-rate per SRU (in N_2 normalized to 1 bar) on a 3x200cm^2 stack with estimation of the inner-leak and associated cell leak-rate per cm^2.

3. Final words

Ensuring gas-tightness in SOE system remains a challenging objective in regards of the involved constraints. However, with the proper definition of leak-rate criteria based on reasonably achievable levels, solutions can be implemented to operate these high temperature systems in safe conditions. A large panel of methods can be used to perform measurement/qualification and monitoring of the gas-tightness of complex objects such as stacks in operating conditions or at RT. Therefore, when designing an SOE system, the initial gas-tightness shall not be considered as the major issue but as a specific function among others. If low leak-rate levels can appear appealing, the gas-tightness is only one of

the keys to achieve high stack performances. A well-designed sealed interface shall of course ensure a reasonably low level of leak-rate, but above all, has to be resilient to the formation of defects without affecting the stack mechanical behaviour. Most of today's long duration tests usually end-up due to strong degradations of the gas-tightness of the stacks, enhancing the mechanical durability of the sealed interfaces are required to challenge the stack performance over time.

Acknowledgements

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