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Benchmark Study of Performances and Durability between Different Stack Technologies for High Temperature Electrolysis

Jerome Aicart ^{1*}, Alexander Surrey ², Lucas Champelovier ¹, Kilian Henault ¹, Chistian Geipel ²,
Oliver Posdziech ², Julie Mougin ¹

¹University Grenoble Alpes – CEA/LITEN, 17 rue des Martyrs, F-38054 Grenoble Cedex 9, France

²Sunfire GmbH, 2 Gasanstaltstraße, D-01237 Dresden, Germany

[] Corresponding author: jerome.aicart@cea.fr*

Abstract

In the current landscape of high temperature electrolysis, mainly two solid oxide cell (SOC) technologies are being used: electrolyte-supported and cathode-supported SOCs. The geometrical differences, namely the thickness of the electrolyte, can lead to vastly different operating temperatures. Since most phenomena affecting performance and durability remain thermally activated, comparing stack technologies can be a difficult endeavor at best.

While the most visible goal of the European project MultiPLHY consists of Sunfire GmbH building the first multi-megawatt solid oxide electrolyzer, a work package is being dedicated to stack testing in a laboratory environment. A harmonized protocol was first elaborated to allow comparing different stack technologies. It includes the recording of performance maps, several galvanostatic steps in thermoneutral conditions, as well as load point and thermal cycles. Subsequently, Sunfire operated a pile-up of two 30-cell electrolyte-supported stacks for over 8,200 hours, while a 25-cell cathode-supported stack was tested at CEA for 6,800 hours.

The present article aims at presenting the findings gathered during the implementation of the protocol. This benchmark study puts forward performance maps as well as voltage and stack temperature profiles over time, and discusses some of the difficulties inherent to long-term testing.

Keywords: Benchmark, High Temperature Electrolysis, Hydrogen Production, Solid Oxide Cell (SOC), Stack.

1 Introduction

The shift to a low-carbon European Union (EU) economy raises the challenges of integrating renewable energy sources (RES) and cutting the CO₂ emissions of energy intensive industries (EII). In this context, hydrogen produced from RES will contribute to decarbonize those industries, as feedstock/fuel/energy storage. According to the International Energy Agency (IEA) [1], only 35 kt of H₂ were produced from electricity via water electrolysis in 2021. Though still quite small, the amount of hydrogen produced via water electrolysis increased by almost 20% compared to 2020, reflecting an accelerating deployment of electrolyzers. According to the pipeline of hydrogen production projects, the annual production of low-emission hydrogen could reach more than 24 Mt H₂ by 2030 [1]. With its RePowerEU plan (affordable, secure and sustainable energy for Europe) [2], Europe will account for a large portion of this capacity, with a renewable H₂ target set to 10 million tons of annual domestic production (~ 100 MW), and an additional 10 million annual tons of imported H₂. Though most of those projects concern Alkaline and Proton Exchange Membrane (PEM) electrolyzers with units at the scale of tens of MW installed, High Temperature Electrolysis (HTE) demonstration units, based on Solid Oxide Cell (SOC) technology, start to reach the MW scale. We can quote the 710 kW_{AC} Grinhy2.0 unit installed on Salzgitter steel plant in Germany in 2020 [3], and the ~2.4 MW_{AC} MultiPLHY unit to be started in 2023. The latter is located in Rotterdam, and its hydrogen production ($\geq 60 \text{ kg h}^{-1}$) will feed the chemical processes of NESTE's renewable products refinery [4].

The Alkaline and PEM electrolyzers can yield overall system efficiencies around 63-70%_{LHV} and 56-63%_{LHV}, respectively [5], and are expected to reach 70% by 2030 [6]. Conversely, the development of Solid Oxide Electrolysis technology is sustained by promises of system efficiencies greater than 85%_{LHV} (assuming waste heat for steam generation), and targeting 90% in 2030 [6]. Such significant efficiency boost compared to the more market-ready technologies is particularly relevant in the current context of high electricity and natural gas prices.

The industrialization efforts for High Temperature Electrolysis (HTE) in Europe are led by Sunfire GmbH. Indeed, the German company accounts for the vast majority of power installed through different generations of systems (e.g. Boeing [7], Grinhy [8], [9] or Grinhy2.0 [3]), in addition to the incoming MultiPLHY one. Remarkably, their 710 kW_{AC} GrInHy2.0 electrolyzer demonstrated an efficiency of 84%_{LHV}. However, additional actors are ramping up their capabilities. Long-time player in the field of SOC, SolydEra (formerly SolidPower) has recently announced through the rebranding a redirection of their focus onto green hydrogen production. Historically interested in electricity production, the Italian-Swiss-German group has installed more than 2,000 micro-combined heat and

power systems (Bluegen, 1.5 kW_{el} [10,11]) and built a highly automated cell/stack production factory. Moreover, Topsoe has announced the construction start of a plant with an impressive manufacturing capacity of 500 MW per year to support their green H₂ production efforts. Lastly, freshly founded in 2021, Genvia is an ambitious joint-venture company by SLB, CEA and other co-investors that installed their pilot production plant in France [12]. Outside of Europe, it is worth noting that UK-based Ceres Power is targeting a 1 MW HTE demonstration plant to be in operation in 2023, and Bloom Energy (USA) has announced a functioning 10 MW HTE for ammonia production for 2023. These announcements highlight a dynamic industrialization of the technology towards the commissioning of (pre-) industrial HTE systems.

The vast majority of the above-mentioned companies either use electrolyte-supported (first generation) or cathode-supported (second generation) cells piled-up in stacks as their core technology. Electrolyte-supported cells rely on thicker electrolytes for mechanical integrity. Therefore, the operating temperature is generally in the 800-850 °C range to reach sufficient current densities. Conversely, cathode-supported cells typically display electrolyte thicknesses in the 2-10 µm range, allowing for lower operating temperatures. Since most physical phenomena occurring in HTE and controlling performance and degradation rates are thermally activated, comparing cell or stack technologies that operate in different temperature ranges can be tricky. The present work thus strives to provide objective elements of comparison in regards to performance and durability through the benchmarking of two stack technologies: one electrolyte-supported stack (ESS) and one cathode-supported stack (CSS). The third generation of (metal-supported) cells, as manufactured by Ceres Power, for example, is out of the scope of this study.

Regardless of cell architecture and due to the overall early stage of industrialization of the technology, the “levelized cost of hydrogen” (LCOH) [13] when produced by HTE remains high. It is however expected to decrease due to the combined effect of higher efficiencies as previously stated, as well as a steep decrease of the capital cost (expected to reach 800 € (kg day⁻¹)⁻¹ by 2030 [6]). Nevertheless, because such cost is currently largely controlled by the stack replacement frequency, degradation rates and subsequent stack lifetimes are crucial characteristics to be assessed when characterizing or benchmarking technologies. The great majority of the degradation data found in the literature has been obtained through galvanostatic operation at a set temperature. Consequently, degradation rates for SOEC operation are typically expressed in terms of voltage increase over time. The following highlights some of the results most relevant to the present study, and obtained over at least 4 kh. At cell level, Schefold et al. [14] notably carried out a durability test of 23 kh on an electrolyte-supported 45 cm² cell from Kerafol, 20 kh of were spent in SOEC mode at -0.9 A cm⁻² and about 850 °C. Voltage

degradation over the operation period was $+7.4 \text{ mV kh}^{-1}$ (or $0.57 \%U \text{ kh}^{-1}$). In another study [15], the same authors reported an impressive 34 kh electrolysis test on a similar cell, at -0.6 A cm^{-2} and 50% SC. While the initial cell temperature was about 780°C , it was later on increased several times to bring the cell voltage down closer to thermoneutral levels. As such, they reported both voltage evolution rates, between $+4$ and $+5 \text{ mV kh}^{-1}$ (or $+0.3$ and $+0.4 \% \text{ kh}^{-1}$) and a temperature compensation rate of $(0.8\text{-}0.9) \text{ K kh}^{-1}$. At short-stack level, Fang et al. [16] operated a cathode-supported 2-cell stack for more than 20 kh, most of which spent in electrolysis mode at 800°C , -0.5 A cm^{-2} and 50% steam conversion (SC). They reported a $\sim 0.6 \%U \text{ kh}^{-1}$ degradation rate. Another (6-cell) short stack was operated for 10.7 kh in electrolysis mode by Rinaldi et al. [17]. The authors reported a $0.5 \%U \text{ kh}^{-1}$ degradation at 720°C , -0.5 to -0.6 A cm^{-2} and a SC from 42% to 50%. For full stacks, Lang et al. [18] tested a 30-cell electrolyte-supported stack (Sunfire GmbH) over a total of 7.5 kh. The 3.4 kh spent in SOEC mode, 820°C , -0.52 A cm^{-2} and 70% SC yielded a combined evolution of $+0.5 \%U \text{ kh}^{-1}$ for the voltage and $+3.0 \text{ K kh}^{-1}$ for the stack temperature. In addition, Corre and Brisse [19] carried out a 9 kh test on a 25-cell CSS operated in the $750\text{-}780^\circ\text{C}$ temperature range with current densities of -0.57 and -0.72 A cm^{-2} and a SC of 50%. They recorded a $2.3 \%U \text{ kh}^{-1}$ degradation rate. Scaling up further the test objects, Peters et al. designed, commissioned and operated a 4-stack (10 layers each) reversible module for more than 9 kh in various conditions, during which a 4 kh steady step in electrolysis mode was carried out at -0.5 A cm^{-2} and approximately 800°C . The corresponding overall degradation rate was $+0.6 \%U \text{ kh}^{-1}$.

2 Experimental

This section describes the intended experimental protocol, the practical deviations during its implementations, as well as the stack geometries and testing equipment.

2.1 Intended Protocol

Since benchmarking different stack technology can be tricky, an attempt at formulating a harmonized protocol was initially made. The outcome is a public deliverable that is available on MultiPLHY project website [4].

Overall, the stacks were maintained at or near the thermoneutral voltage. To do so, the stack temperature was increased over time to compensate degradation [20–23]. While such operational strategy has been suggested by Hansen et al. [24] to maintain electrical output in SOFC mode, and later on by Corre & Brisse [19] to extend electrolysis operation, an additional objective here was to avoid thermal gradient throughout the stacks that could negatively impact stack stability and/or degradation rates [23]. Whenever applicable, a SC of 70% was adopted, and a small proportion of H₂ was systematically added to the inlet steam to protect the Nickel (Ni) comprising the fuel electrodes cermet from oxidizing (5–10 vol.% H₂). A current ramp rate of 0.06 (A cm⁻²) min⁻¹ was targeted, as per SOCTESQA recommendation [25].

The protocol started by performing an Electrochemical Tightness Test (ETT), consisting in switching off inlet gas supply from a dry H₂ and air initial state, and recording the rate of voltage drop over time. This test is rather drastic, yet much more efficient in detecting tightness defects than a collection rate assessed through flowrate measurements. The ETT ended either when a voltage measurements passed below a threshold of approx. 0.8 V, or after 20 minutes, whichever came first.

Then, an initial performance map was recorded in order to compare the stacks' performances. For different targeted stack operating temperatures (Table 1), the stacks were polarized from open circuit voltage (OCV) to the thermoneutral voltage to record their performances. From there, if needed, current and flowrates were adjusted incrementally until stack operation resulted in observing simultaneously (i) an average cell voltage of ≈1.29–1.30 V (depending on the temperature), (ii) 70% SC, and (iii) temperature under load ≈ temperature at OCV. These conditions and the corresponding current densities will be referred to in the following as THN70 and i_{THN70} , respectively. A second and final performance map was also recorded at the end of the testing sequences.

Stack stability over time was then assessed through two segments of galvanostatic operation over a minimum of 1,000 h each at different current densities. After a first step at -0.65 A cm^{-2} , the CSS targeted -0.85 A cm^{-2} while the ESS aimed for -0.5 A cm^{-2} . Subsequently, load point cycles were investigated through 500 h of 5h-on (-0.5 A cm^{-2} for both stacks), 5h-off load cycles under constant gas flowrate and composition. At the end of this procedure, a steady-state step of up to 500 h at -0.5 A cm^{-2} was performed to allow for possible recovery of the cell performances.

Finally, the stacks had to experience at least two thermal cycles, and one thermo-redox cycle at the end of the overall testing sequence, during which the stacks were cooled down without safety gases in order to simulate an uncontrolled shutdown. All in all, the strict implementation of this protocol would last 3.5 to 4 kh.

2.2 Test of Cathode-Supported Stack

2.2.1 Stack Description

Commercial $12 \times 12 \text{ cm}^2$ electrode-supported cells with an active area of 100 cm^2 were used in this work. All cells were of the same design, exhibiting a Ni and 8 vol.% yttrium-stabilized zirconia (8YSZ) cermet fuel electrode, an 8YSZ electrolyte, a cerium gadolinium oxide (CGO) diffusion barrier, and a lanthanum strontium cobalt (LSC) oxygen electrode.

The 25-cell stack incorporated thin AISI441 ferritic stainless steel interconnects with proprietary design, allowing for cross-flow operation. Due to optimizations of the gas distribution, achievable conversion rates have been significantly increased in recent years [26]. Tightness between compartments was achieved with a combination of ceramic glass seals, mica foils, and an integrated stand-alone clamping system for mechanical load [27]. Finally, electrical contacts between electrodes and interconnects were insured through nickel grids on the hydrogen side, and lanthanum strontium manganese (LSM) on the oxygen side. The stack gas connections to the test bench were done through an in-house developed solution based on a proprietary form of high temperature flanges [28]. Additional information on stack design and experimental results on performance and durability can be found in references [13,29–34].

2.2.2 Testing Equipment and Deviations from the Protocol

Stack assembly from in-house manufactured components, as well as glass formation and cermet reduction procedures, were carried out on a dedicated stack conditioning bench co-developed between company ECM and CEA. Subsequently, it was transferred to an electrolysis/fuel cell reversible lab system (Figure 1a) incorporating some balance of plant (BoP) components, such as heat exchangers for heat recuperation, for the actual test sequence. Details about the testing equipment can be found elsewhere [32,35,36].

The drop-down furnace incorporated one lateral heating element and another one on top. It was positioned above the rest of the bench BoP components. To overcome the known vertical (top-to-bottom) temperature gradient in the furnace, which could jeopardize isothermal operation, the stack was manufactured with an integrated stack heating solution (ISHS) [32]. Unfortunately, the bottom part of the ISHS gave out at around 300 °C during the first temperature ramp up sequence. The subsequent inability to measure the resistance of the heating element suggests that the manufacturing process may have introduced an air bubble in between the heating element and the electrical insulation material surrounding it. This would have led to extreme local temperatures due to the inability to efficiently extract heat by conduction, and led to the destruction of the heating element and the opening up of the electrical circuit. To overcome this, a high temperature heating wire (maximum temperature 900 °C) was wrapped around the inlet gas preheating loops as well as the stack bottom self-clamping element. The overall thermal regulation of the furnace was modified so that only the lateral furnace element was used for temperature control, while the power delivered by the wrapped heating wire was adjusted to nullify the temperature difference between the top and bottom parts of the stack. While quite rudimentary, the implemented final solution led to acceptable results in terms of performance and temperature control. It has remained functional throughout the complete testing sequence.

While performance assessment at 800 °C was initially targeted, a maximum stack temperature of only about 765 °C could be reached due to the degraded thermal management as described above. Also, the current ramp rate was increased from 0.06 to 1 (A cm⁻²) min⁻¹. This fast control strategy, successfully implemented in previous works [23,37], allowed avoiding significant temperature gradients in the stack when ramping up the stack voltage between OCV and thermoneutral voltage. Finally, no redox cycle was done on the stack, since it was believed it could cause damage that would have hindered post-mortem analyses.

2.3 Test of Electrolyte-Supported Stacks

2.3.1 Stack Description

Sunfire's standard ESS consists of 30 layers as described in previous publications [38–40]. Typically, two of these stacks are piled up and tested together (Figure 1b) at the Sunfire test field. The employed electrolyte supported cells (ESC) consist of an 80 μm thick 3YSZ electrolyte, a Ni and gadolinium-doped ceria (GDC) hydrogen electrode, and a lanthanum strontium cobalt ferrite (LSCF) & GDC oxygen electrode. The cells exhibit an active area of 127.8 cm^2 . The interconnect is a steel cassette out of Crofer 22 APU with a manganese-cobalt-iron (MCF) coating at the oxygen side. The steam/hydrogen mixture is distributed to each layer via internal manifolds, whereas the air side has an open manifold, allowing for a co-flow operation.

2.3.2 Testing Equipment and Deviations from the Protocol

For the reported test, a FuelCon test bench was used, where a so-called “Stack-Test-Box” (STB) designed by Sunfire is mounted in. In this STB, the two stacks are integrated by applying the necessary clamping force, thermally insulating the stacks, and guiding the gases and air through the stacks. No active heating elements are used in the STB, but the stacks are heated by hot air and gases up to 840 $^{\circ}\text{C}$.

Additionally to the defined test protocol, the galvanostatic operation was performed at 70% and 80% steam conversion. The stationary operation has only been done at -0.5 A cm^{-2} , not at -0.65 A cm^{-2} due to higher than expected area specific resistance (ASR), maybe caused by higher initial degradation due to high initial silica contamination, or cells batches with higher ASR.

3 Results and Discussion

3.1 Overview and Time Evolutions

Figure 2 shows the evolution of stack current, voltage, and temperature for both technologies over the complete test sequences. The CSS temperature is defined here as the outlet air (OA) temperature, while for the ESS, with their open air compartments, the data relates to the maximum temperature recorded among several sensors inserted inside the stack. A 1,200 h gap is visible on the CSS test, mostly linked to the building scheduled annual technical shutdown. It is important to note that aside from the load point cycles, each segment of the protocol is characterized by a steady current (H_2 production) and a steady stack voltage (electrical consumption at stack level).

Over the initial 1,500 h or so of CSS operation, rapid evolution of the furnace temperature was necessary to maintain thermoneutral conditions, from the initial 672 $^{\circ}\text{C}$ to approximately 730 $^{\circ}\text{C}$. Such

overall behavior is consistent with several reports of the literature [34,41]. Throughout the testing sequence, the stack underwent two thermal cycles (at approximatively 1.5 & 4 kh), with stack operating conditions being the same before and after to assess potential impacts. These chronologically led to +3 °C and a +1.5 °C temperature increases. Beyond the numerical results (surely affected by experimental imprecisions) the impact of the cycles on the performance remained limited. Due to the imprecise thermal regulation of the furnace, some slight deviation from the thermoneutral voltage is visible throughout the point load cycles section of the protocol. However, this had no noted consequences on performances or durability. Voluntarily excluding the initial stabilization period, linear regressions were carried out between points ① and ② (Figure 2a – 3,100 h segment), as well as between points ② and ③ (2,100 h segment), all points corresponding to stable operation at -0.65 A cm⁻². The rates of temperature increase over time hence calculated were +2.3 K kh⁻¹ and +12.4 K kh⁻¹, respectively. It should be noted that this last rate is quite comparable to what has been reported by Corre & Brisse (+14 K kh⁻¹ at -0.57 A cm⁻² [19]).

The ESS went through several unwanted events between 3 and 5 kh, caused by failures of the steam supply, and leading to thermal cycles. These events are discussed in section 3.3. As previously stated, and as shown in Figure 2b, operation at -0.65 A cm⁻² led to a thermoneutral temperature too close to 860 °C to allow sustained operation over extended durations. When tested in the STB, the two stacks were heated through air and polarization. Consequently, and contrary to the CSS, point load cycles also led to temperature fluctuations. Normalizing the stack temperature evolutions over 8 kh yields overall rates of +3.9 and +4.4 K kh⁻¹ for the two stacks.

The above results show that after 7,900 h, the ESS was closing in on the maximum acceptable temperature. Consequently, had the test continued, the current density would have had to be decreased over time. Contrastingly, after about 6,800 h, only about 760 °C were necessary to maintain operation of the CSS at -0.65 A cm⁻². Extrapolation of the temperature profile suggests a significant remaining lifetime at iso-performance, due to the stack low “beginning-of-life” (BoL) temperature. Indeed, assuming a maximum theoretical “end-of-life” (EoL) temperature of 860 °C due to the glass seals, the rate of temperature increase recorded in the later part of the test sequence (+12.4 K kh⁻¹), akin to a degradation rate, translates into approximatively 15 kh total expected stack lifespan at iso-performances. Conversely, extrapolating from the +2.3 K kh⁻¹ rate translates into a 60 kh lifetime. While the main driver for degradation may have changed between the two segments to explain the vastly different recorded rates, these results highlight at the very least the necessity of actual testing beyond 5 kh to evaluate stack replacement frequency and properly estimate a consolidated LCOH.

In reality, AISI441 alloy would not be expected to handle such EoL temperature as well as Crofer, for example, likely resulting in shortening stack operation. It should be noted that degradation of the CSS at temperatures above 800°C is the subject of on-going investigations. Indeed, a better understanding of the stability of AISI441 alloy in an operating stack over the 800-860°C temperature range, likely dependent on the implementation of efficient interconnect coatings, could allow identifying an optimal EoL temperature that maximizes the H₂ output over the stack lifetime.

It is important to underline that extrapolation does not equate practical demonstration. In this view, the ESS has shown it can be operated for more than 8,000 h at iso-performance without experiencing sudden, accelerated degradation drivers or catastrophic failures that would have precipitated the stack's EoL. Such statement can only be made up to 6,800 h for the CSS, as the corresponding test cannot rule out accelerated degradation or sudden failure beyond 7 kh.

Throughout the complete duration of both experiments, the temperature-adapting strategy led to iso-performance operation and no production loss or increased voltage were recorded. To emphasize this further, Figure 3 showcases the evolutions of electrical consumption for H₂ production at stack level (DC power-to-H₂). Results, only dependent on the operating voltage and not the current density, are indeed stable over time. They are mostly comprised between 34.5 and 35.5 kWh kgH₂⁻¹, the difference being explained by the slight thermoneutral voltage dependence on the temperature. Such range of electrical consumptions is to be expected with any solid oxide stack technology being operated at the thermoneutral voltage, and is therefore unsurprisingly consistent with previously reported data [37]. These results can be compared to 46-48 and 51-54 kWh kgH₂⁻¹ for PEM and alkaline electrolyses, respectively (assuming operating voltages of 1.7-1.8 V and 1.9-2 V, respectively [42]). Had the CSS and ESS tests continued until their respective EoL temperatures are reached, current densities would then have had to be gradually decreased over time to compensate degradation while stabilizing stack temperatures. This necessary EoL operating strategy would however induce gradual production loss as well as decrease module efficiency, both driving H₂ production costs up.

3.2 Performance Maps

At the start and the end of the overall testing sequences, performance maps have been recorded. Figure 4 gathers the i_{THN70} results (cf. section 2.1) recorded on the CSS and the ESS throughout this work. It

is worth noting that contrary to standard polarization curves, each point along such a performance curve corresponds to stable and relevant operating conditions at a given time.

As expected, the cathode-supported stack (CSS) could reach higher current densities at lower temperatures compared to the electrolyte-supported stack (ESS). For example, the initial performance map indicates that 840 °C was necessary for the ESS to reach -0.59 A cm^{-2} in THN70 conditions while the corresponding temperature for the CSS was lower than 670 °C, a difference closing in on 200 °C. Additionally, the ESS could not be steadily operated at -0.65 A cm^{-2} due to the resulting temperatures too close to the acceptable upper limit, while a thermoneutral current density of -1.55 A cm^{-2} was initially recorded on the CSS at 763 °C.

Comparing the initial and final performances also show that in comparable conditions of temperature, the CSS experienced a significant decrease of thermoneutral current densities over time. For example, at about 703 °C, the current density allowing (near) isothermal stack operation and 70% steam conversion decreased from -0.83 to -0.30 A cm^{-2} , a 63% drop. The extent of the recorded performance drop decreased at higher temperature, going from -1.55 down to -0.65 A cm^{-2} at approximately 765 °C (-58%). The same trend is also noticeable on the ESS, albeit to a lesser extent. Indeed, thermoneutral current densities went from -0.34 down to -0.23 A cm^{-2} at 780 °C (-32%), and from -0.59 to -0.45 A cm^{-2} at 840 °C (-24%). These results show that the drop in thermoneutral current densities over time, akin to “apparent” degradation, decreases when the performance comparison is carried out at higher temperature. Conversely, the temperature of the measurement does not impact intrinsic stack degradation.

When normalizing the above performance drops in respect to duration at comparable temperatures, the degradation rate for CSS at 765 °C is approximatively $8.5\% \text{ kh}^{-1}$, while that of the ESS at 780 °C is about $4.1\% \text{ kh}^{-1}$. At 840 °C, a more relevant temperature for the ESS, the degradation rate is $3.0\% \text{ kh}^{-1}$. Consequently, when the cell/stack temperature evolves over time, degradation should be evaluated in regards to a reference temperature [43-44]. Another way to interpret this result would be to say that ‘the rate of temperature increase over time’ (when maintaining thermoneutral operation) decreases with higher temperatures. This can be explained by the non-linear temperature dependence of the ASR, which can be expressed by an Arrhenius function in the form given by Equation (1):

$$ASR = R_0 e^{\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right)} + R_c \quad (1)$$

with a pre-exponential factor R_0 , a constant-over-time activation energy E_A in J mol^{-1} , R the gas constant in $\text{J K}^{-1} \text{mol}^{-1}$ a reference temperature T_{ref} , and a temperature-independent offset R_c . Based on both stack tests, it is clear that this nonlinearity increases due to degradation, meaning that mainly R_0 increases and not R_c . Hence, at lower temperature, the impact of apparent degradation is larger than at higher temperatures. It must not be misinterpreted in the way that the ASR degradation would be lower at higher temperature. The following Figure 5 visualizes this argumentation. Here, either R_0 or R_c is increased by the same amount ΔR . Only at the reference temperature are the degraded ASRs equal. If only R_c increases, the ASR degradation would be almost the same for all temperatures, but if R_0 increases, the observed stacks performance can be explained: the performance drop compared to a reference state would be higher if checked at lower temperature. In reality, both parameters are likely to increase over time, with R_0 being the dominant one. This applies to both investigated stack technologies, CSS and ESS.

As stated, the recorded decrease of CSS performance over time at iso-temperature is quite significant, especially considering the stack was “only” in operation for a few thousand hours. Such impact on the performances would be consistent with degradation rates of several percent per thousand hours typically reported on electrode-supported cells operated in electrolysis and galvanostatic modes [45]. However, because of the operational strategy of increasing the temperature over time, extrapolative results presented in this work indicate that the stack may have still been operable for quite some time before reaching its EoL temperature (around 860°C). This highlights that the typical notion of degradation rates measured during potentiostatic or galvanostatic operation at iso-temperature may not be fully representative when trying to evaluate the lifespan of a cell/stack, especially when a thermoneutral operating strategy is favoured.

3.3 Discussion on Difficulties and Requirements for Long-Term Durability Tests

At approximately 3,400 h, CEA’s laboratory experienced a cut-off of the H_2 supply, consequence of a problem with the ambient air extraction. The polarized stack was consequently fed with 100% steam. The gas supply then was abruptly restored after 3h30, while the H_2 mass flow controller’s valve had remained fully open. This led to a +300 mbar overpressure event at the bench inlet, approximatively,

as seen in Figure 6 (the exact position of the pressure sensors that recorded the event can be found in [36]). Table 2 gathers OCV values measured throughout the test protocol via the eight voltage measurements available on the test bench. As can be seen, no significant impact of neither the loss of the H₂ supply, leading to pure steam operation, nor the subsequent water head event can be noticed on the stack voltage and OCVs.

Between 3,000 and 5,000 h approximatively, the ESS experienced several unplanned malfunctions of the steam supply, leading to temporary starvation and unwanted thermal cycles (Figure 2b). While the short-term performance was impacted, with a noticeably higher thermoneutral temperature at the targeted current density, the stacks proved to be resilient, and their response improved rapidly. No significant residual performance drop was consequently recorded. In addition, as part of the protocol, the ESS underwent two electrochemical tightness tests (ETT), during which all gas supplies to the stacks were cut-off and the subsequent evolution of blocks of cell voltages over time was recorded. Figure 6 shows the initial ETT results, and the final ones recorded after the thermo-redox cycle. The results highlight excellent tightness, and the stack's ability to withstand the overall test sequence in addition to one thermo-redox cycle (as defined in the protocol) without severely compromising the integrity or performances of the cells. Indeed, the tests ended due to reaching the time limit, and not the voltage threshold. The faster voltage drops recorded for 3 blocks of cells indicate small leaks, which were originally caused by the mentioned malfunctions between about 3,000 and 5,000 h. These events outside of the specified operation points must be avoided to ensure an ideal long-term operation of the stack. Nonetheless, the present leaks did not endanger the further operation and the successful completion of the test. The excellent ability to withstand the thermo-redox test demonstrated by the ESS is particularly relevant. Indeed, stacks would likely undergo such a severe transient profile in case of an emergency shutdown if no (potentially costly) safety concept involving forming gas is implemented at system level.

Overall, both stacks showed excellent resilience and came out relatively unscathed of the different malfunctions and failure modes that occurred during their respective tests. This paragraph only details some of the unwanted events that occurred during both testing sequences. While not meant to be exhaustive, these examples nevertheless underline the difficulties inherent to long term testing, in spite of CEA and Sunfire extensive testing experience. They also highlight the need to have stacks tolerant enough, by design, to such problems and malfunctions that will inevitably occur in industrial units.

4 Conclusions

In order to benchmark a cathode-supported stack (CSS) and an electrolyte-supported stack (ESS), a harmonized protocol was formulated and implemented in this work. Subsequently, Sunfire tested 2-30 cell ESS piled-up for 8,200 h, and CEA tested a 25-cell CSS for 6,800 h. The gathered experimental observations were presented, and some elements of comparison between the two stack technologies were provided.

Performance wise, as expected, the CSS could reach much higher current densities at lower temperature. To reach similar performances on both stacks, the temperature difference was closing in on 200 °C at the start of the tests, and 100 °C at the end. Significant decrease in performances was recorded on both stack technologies over the testing sequences. The extent of the measured performance drop decreased with higher temperatures, emphasizing the importance of that parameter when assessing degradation.

The ESS was operated for more than 8,200 h at iso-performance, -0.5 A cm^{-2} and 70% steam conversion (SC). Over that time, the temperature was gradually increased to compensate degradation and maintain the stack near an isothermal state, to end up close to the maximum allowed temperature. Normalization of the recorded decrease of thermoneutral current density over time leads to a calculated degradation rate of $3.0\% \text{ kh}^{-1}$ at 840 °C. After about 6,800 h, the CSS thermoneutral temperature associated to -0.65 A cm^{-2} and 70% SC was 760 °C. Despite a significant calculated degradation rate of $8.5\% \text{ kh}^{-1}$ at 765 °C, the extrapolated maximum lifetime at iso-performances was greater than 15 kh due to the low beginning-of-life temperature (672 °C). This work thus demonstrates that the stacks lifetime can be vastly extended through the adopted operational strategy, all-the-while sustaining performances. Indeed, over their respective test sequences, both stacks maintained production targets and no hydrogen production loss was recorded.

This work also highlighted some of the technical difficulties inherent to long term testing. Emergency shutdowns happened, and test bench components failed. In this view, both stacks showed sufficient resilience and remained relatively unscathed through all events. In addition, the ESS was left mostly unaffected by a thermos-redox cycle, which could translate in easier system design and integration.

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For Peer Review

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Tables

Targeted temperature / °C	700	750	770	800	830	850
Stack technology	Cathode-supported stack			N.A.		
	N.A.			Electrolyte-supported stack		

Table 1: Targeted temperatures for the recordings of performance maps for both stack technologies.

Time / h	U ₁ / mV	U ₂₋₄ / mV	U ₅₋₈ / mV	U ₉₋₁₂ / mV	U ₁₃₋₁₆ / mV	U ₁₇₋₂₀ / mV	U ₂₁₋₂₄ / mV	U ₂₅ / mV	T _{OA} / °C	OCV _{TH} / mV	Δ _{TOT} / %
292	888	887	888	888	887	887	888	888	673	892	-0.51%
2,642	870	868	869	869	868	868	868	867	717	873	-0.51%
4,728	870	871	871	871	870	871	872	872	714	875	-0.48%
5,825	854	855	855	855	854	854	854	854	753	859	-0.53%

Table 2: Evolution of OCVs (or average OCVs for packs of 3 or 4 cells) over time for the CSS, as recorded by the eight voltage measurements available of the test bench. OCV_{TH} denotes the theoretical OCV accounting for the changing stack temperature T_{OA} taken as the Outlet Air (OA) temperature, and Δ_{TOT} the deviation of the OCV at stack level from OCV_{TH}.

Figure Captions

Figure 1: a) stack used at CEA [35], and b) two-stack pile up installation at Sunfire.

Figure 2: Time evolutions for stack current and voltage for the cathode-supported stack (a. to c.) and the two electrolyte-supported stacks (d. to f.). The maximum temperature of both ESS piled-up is shown (solid and doted curves).

Figure 3: Evolutions of DC power-to-H₂ consumption for the cathode-supported stack (CSS) and the electrolyte-supported stack (ESS).

Figure 4: Initial and final performance maps recorded on both stack technologies. THN70 relates to operation at the thermoneutral voltage and at 70% steam conversion.

Figure 5: Influence of pre-exponential factor R_0 degradation and offset resistance R_C degradation on a temperature-dependent Area Specific Resistance (ASR) expressed by an Arrhenius function (Equation (1)).

Figure 6: Resilience of both technologies with the CSS response to a temporary cut-off and subsequent abrupt restoration of the H₂ supply (a. and b.), leading to an overpressure event, and the electrochemical tightness test (ETT) results recorded on the ESS c) at the start and d) at the end of test including a thermos-redox cycle.

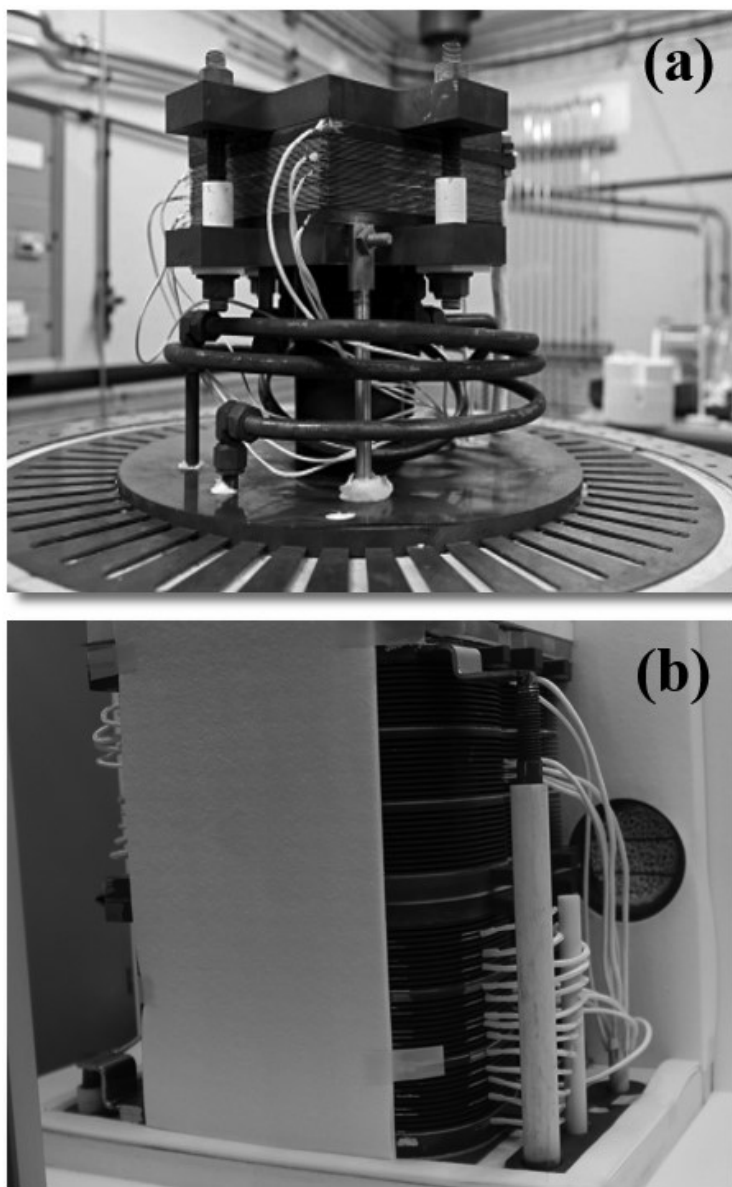


Figure 1: a) stack used at CEA [35], and b) two-stack pile up installation at Sunfire.

39x61mm (300 x 300 DPI)

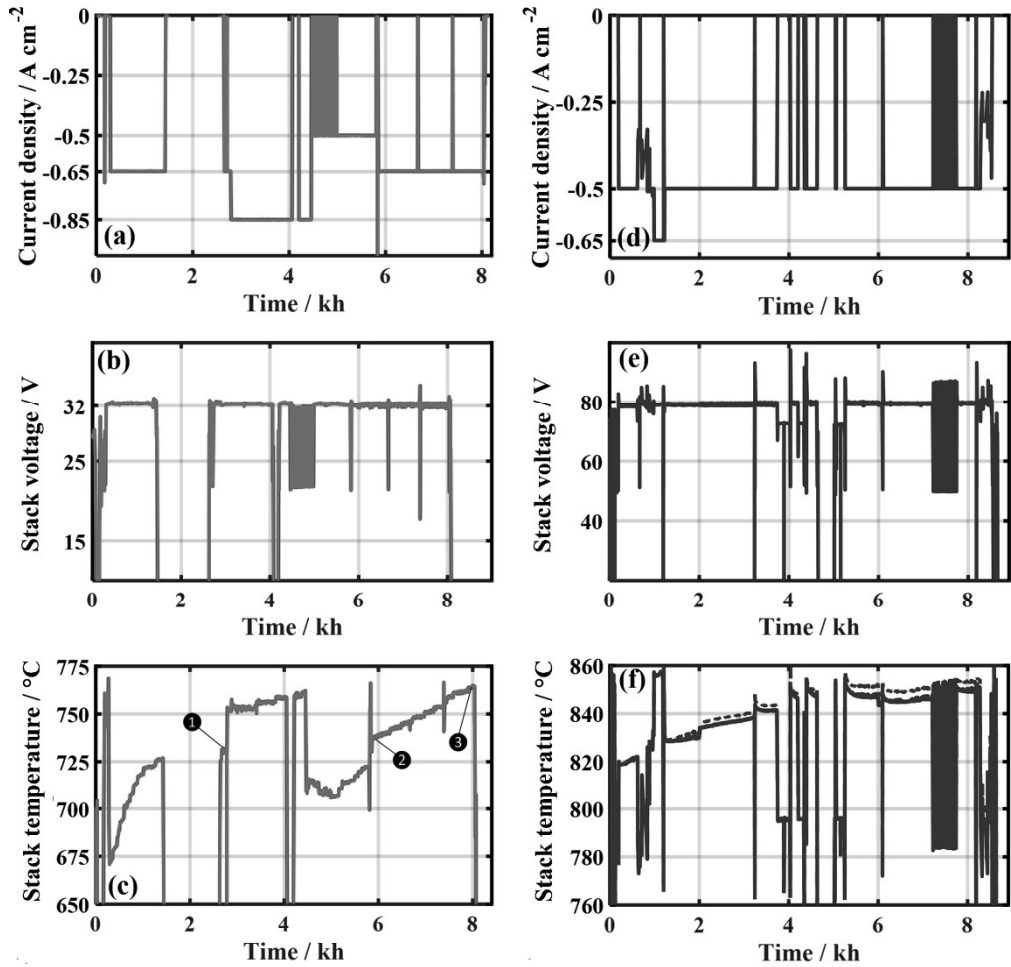


Figure 2: Time evolutions for stack current and voltage for the cathode-supported stack (a. to c.) and the two electrolyte-supported stacks (d. to f.). The maximum temperature of both ESS piled-up is shown (solid and dotted curves).

174x167mm (353 x 353 DPI)

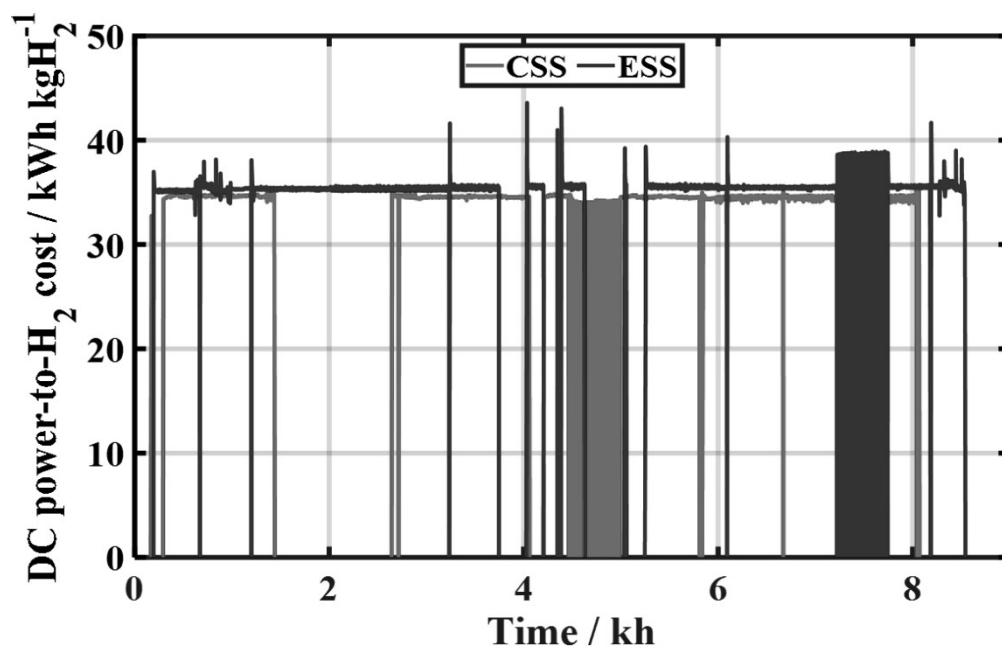


Figure 3: Evolutions of DC power-to-H₂ consumption for the cathode-supported stack (CSS) and the electrolyte-supported stack (ESS).

85x54mm (344 x 344 DPI)

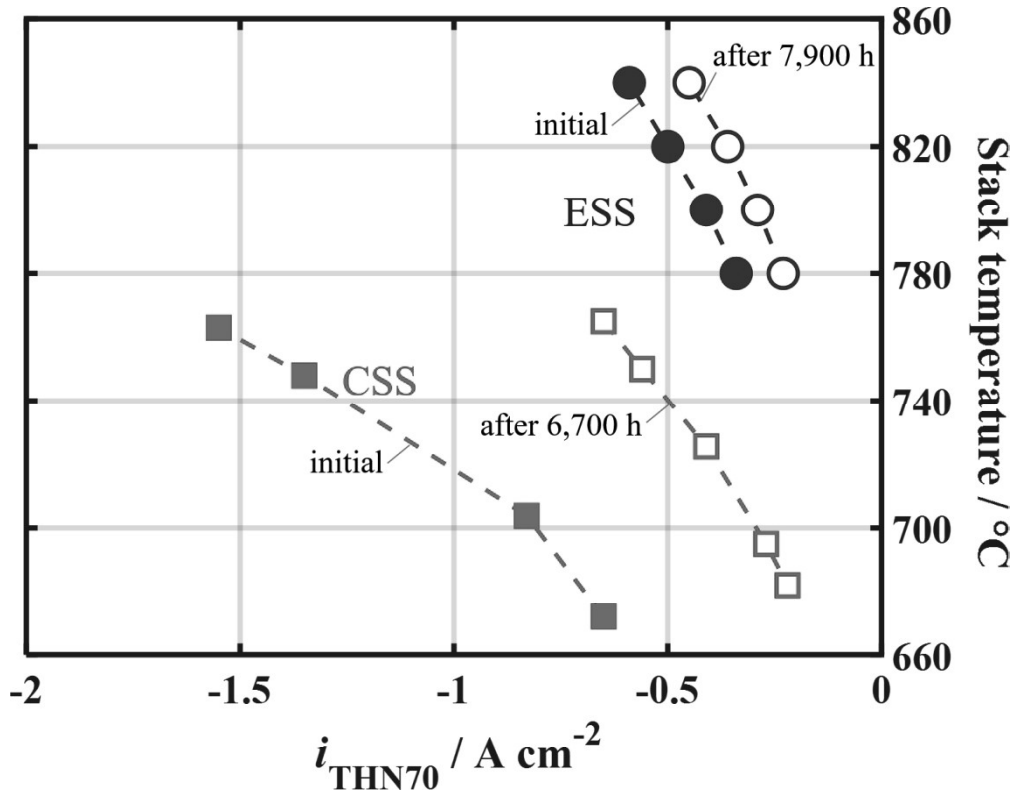


Figure 4: Initial and final performance maps recorded on both stack technologies. THN70 relates to operation at the thermoneutral voltage and at 70% steam conversion.

85x67mm (463 x 463 DPI)

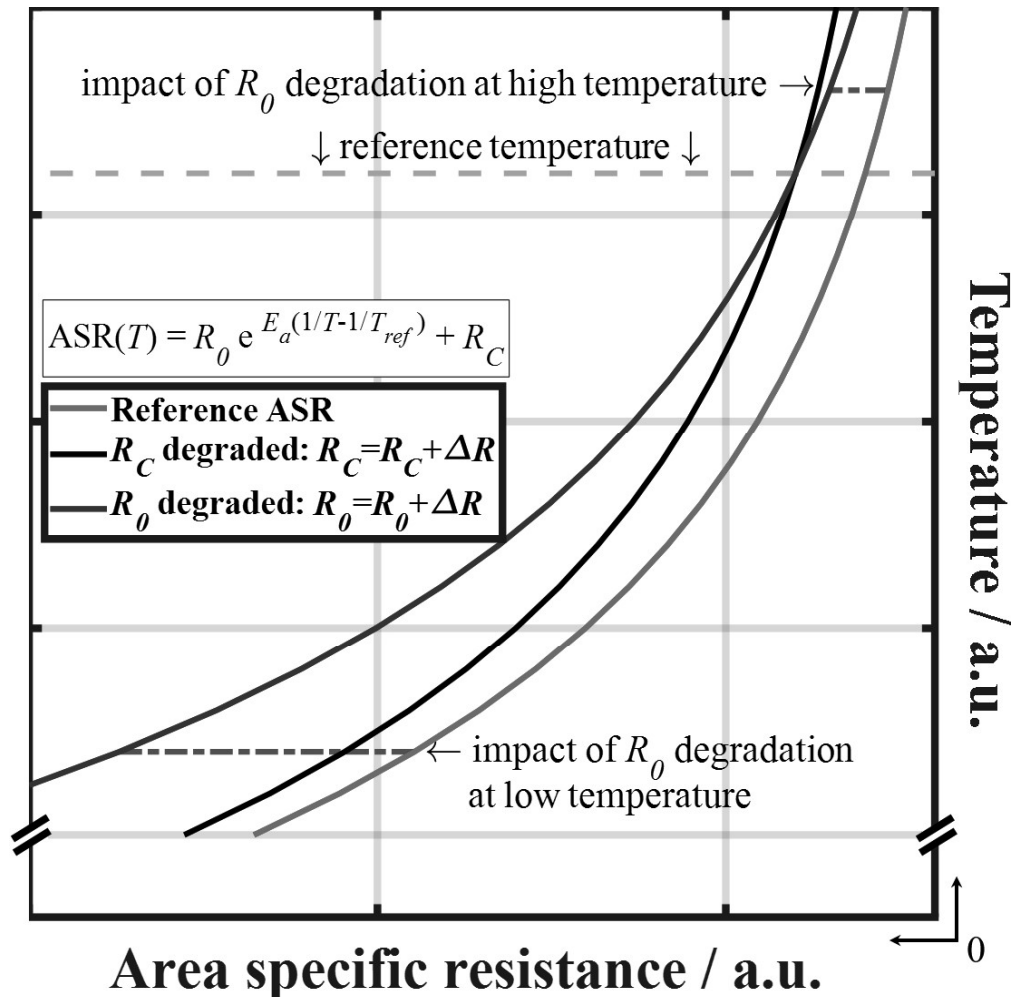


Figure 5: Influence of pre-exponential factor R_0 degradation and offset resistance R_C degradation on a temperature-dependent Area Specific Resistance (ASR) expressed by an Arrhenius function (Equation (1)).

86x84mm (326 x 326 DPI)

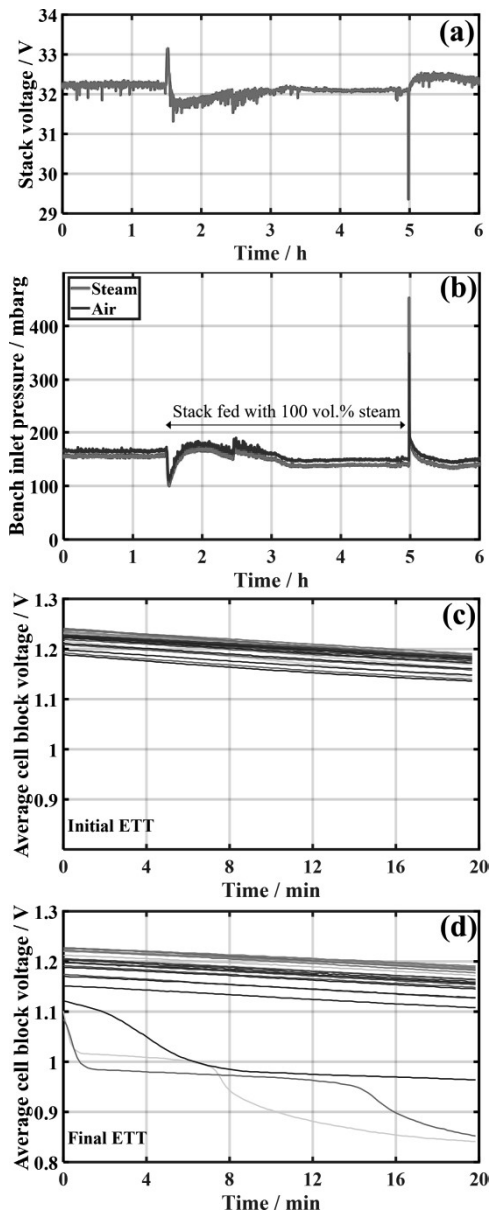


Figure 6: Resilience of both technologies with the CSS response to a temporary cut-off and subsequent abrupt restoration of the H₂ supply (a. and b.), leading to an overpressure event, and the electrochemical tightness test (ETT) results recorded on the ESS c) at the start and d) at the end of test including a thermos-redox cycle.

86x215mm (460 x 460 DPI)