MULTIPLHY

Multimegawatt high-temperature electrolyser to generate green hydrogen for production of high-quality biofuels

"Definition of Testing Protocols"
Deliverable D2.1

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Abstract

The MULTIPLHY project aims at demonstrating the technological and industrial leadership of the European Union in Solid Oxide Electrolysis (SOE) technology by implementing a multi-MW system at a biofuels refinery. Work Package 2 is focused on stack testing in laboratory environment, benchmarking different technologies, and achieving a 25,000 h operating time milestone. The present public deliverable details the experimental protocol under which the stacks will be tested. A special attention has been given to harmonize the testing, despite the sometimes vastly different operating conditions arising from specific cell architectures in the different stack technologies tested.

The protocol includes the recording of performance maps, load-point and thermal cycles, as well as steady-state steps to assess degradation and therefore the expected life-time of three different SOE stack technologies operated exclusively in electrolysis mode.

Introduction

The shift to a low-carbon EU economy raises the challenge of integrating renewable energy sources (RES) and cutting the CO_2 emissions of energy intensive industries (EII). In this context, hydrogen produced from RES will contribute to decarbonize those industries, as feedstock/fuel/energy storage. MULTIPLHY thus aims to install, integrate and operate the world's first high-temperature electrolyser (HTE) system in multi-megawatt-scale (~2.4 MW), at a refinery of biofuels in Rotterdam to produce hydrogen (≥ 60 kg/h) for the refinery's processes.

MULTIPLHY offers the unique opportunity to demonstrate the technological and industrial leadership of the EU in Solid Oxide Electrolysis (SOE) technology. With its rated electrical connection of ~3.5 $MW_{el,AC,BOL}$, electrical rated nominal power of ~2.6 $MW_{el,AC}$ and a hydrogen production rate ≥ 670 $Nm^3.h^{-1}$, this HTE will cover ~1 % of the current average hydrogen demand of the biofuels refinery. This leads to GHG emission reductions of ~8,000 tonnes during the planned minimum HTE operation time (16,000 h). MULTIPLHY's electrical efficiency (85 $\%_{el,LHV}$) will be at least 20 % higher than efficiencies of low temperature electrolysers, enabling the cutting of operational costs and the reduction of the connected load at the refinery and hence the impact on the local power grid.

A multidisciplinary consortium gathers NESTE (a Green Refiner as end-user), ENGIE (a global energy system integrator & operator), PaulWurth (Engineering Procurement Construction Company for hydrogen processing units), Sunfire (HTE technology provider) and the world-class RTO CEA. They focus on operation under realistic conditions and market frameworks to enable the commercialisation of the HTE technology. By demonstrating reliable system operation with a proven availability of ≥ 98 %, complemented by a benchmark study for stacks in the 10 kW range, critical questions regarding durability, robustness, degradation as well as service and maintenance are addressed.

This public deliverable focuses on the benchmarking of different stack technologies via short-term release tests, and details the experimental protocol under which these stacks will be evaluated. Three technologies are being considered: one incorporating electrolyte-supported cells (ESC) by Sunfire, one with cathode-supported cells (CSC) by CEA, and a third one purchased by a procurement to a commercial stack manufacturer. Despite the different operating conditions inherent to the type of cells used, special efforts have been devoted to formulate a harmonized protocol that will enable direct comparison of performances and degradation rates.

1. Overview

In T2.2, three stack technologies will be benchmarked: one incorporating cathode-supported cells (CSC) from CEA, one with electrolyte-supported cells by Sunfire, and a commercial third party stack. CSC rely on thick porous steam electrodes to provide the cells with mechanical support, while ESC are comprised of thick electrolytes. The choice of cell architecture and materials affects nominal current densities, and dictates the operating temperature at the beginning-of-life of the stack: CSCs are typically operated around 700-750°C, and ESCs around 800-850°C. Despite these differences, a special attention has been devoted to formulate a harmonized protocol that will allow comparing the performances and the degradation rate of the stack technologies.

As per the Grand Agreement, the experimental protocol that is to be implemented in T2.2 will include the following steps, given here in chronological order:

- Start-up procedure and initial evaluation
- Initial performance map
- Durability steps in galvanostatic and quasi-potentiostatic operation (i.e. constant DC current and rising thermoneutral temperature due to degradation resulting in a constant cell voltage)
- Load point cycles
- Thermal cycles
- Final performance map
- Final evaluation and shut-down procedure
- If possible, a redox cycle

Additionally the robustness of the stacks will be evaluated by recording geometrical deformations after the SOE operation and the occurrence of any cell breakages. For this the stack manufactures will specify the allowed maximal pressure difference between H_2 and air compartments.

In the following, paragraph 2 will detail the different gas conditions considered, while paragraph 3 will give technical details on the different steps of the protocol.

2. Harmonized Gas Conditions

Despite the widely proven ability for Solid Oxide Cells (SOCs) to be operated both in electrolysis mode and in fuel cell mode, the focus of the MULTIPLHY project is on electrolysis only. Due to the high operating temperatures (i.e. 700-850°C), all water will be in the form of steam. A small proportion of H_2 (5-10 vol%) will systematically be added to the inlet gas flow to prevent oxidation of Nickel particles, constituting of the steam electrodes.

The steam conversion is defined as the quantity of steam electrochemically converted into H_2, over that fed at the stack inlet. This operating parameter is proportional to the electrolysis current. Whenever in operation (i.e. DC current is supplied to the stacks), the steam flowrate will be adjusted so that the steam conversion is equal to 70%.

In addition, neutral gas conditions are defined. During stack temperature ramps (start-up, shutdown, thermal cycle) and in case of emergencies, the steam electrodes will be fed with a mixture of 3 to 5 vol% H_2 balance N_2. The flowrate to be used will be defined by each stack manufacturer.

Throughout the entire protocol, the oxygen electrodes of the stacks will be supplied with air. The air flowrate will be defined by each stack manufacturer. Considering the scale up of the SOE technology to multi-megawatts, a minimal air flowrate is targeted. Under the test conditions, an air flowrate comparable to the steam flowrate is typically used.

3. The Different Steps of the Protocol

3.1 Start-up Procedure and Initial Evaluation

The stacks will be brought from ambient to high temperature in safety gas conditions, as defined in the previous paragraph. The temperature ramp rate will be defined by each stack manufacturer, and is comprised between 0.5 and 4 $°C.min^{-1}$.

The initial evaluation is mainly aimed at quantifying the tightness of the fuel compartments, and will be done by following the voltage drop over time in the absence of gas flows: once the stacks are thermally stable at the initial operation temperature, the H_2 content in the inlet flow and/or the flowrate of 5 vol% H_2 balance N_2 will be increased so that all cell voltages are above 1.1 V. Upon cell voltage stabilization, all inlet flowrates will be interrupted, while monitoring the evolution of cell voltages. As O_2 from the surrounding air slowly makes its way into the steam electrode compartments, due to cracks and defects in the seals, if any, the voltages will drop. The rate of voltage drop will allow quantifying the tightness of the seals. The test will conclude after 20 min, or when any cell voltage drops below 0.8 V.

Following the tightness test, the stack will be operated in steady state. This conditioning-like step will last until voltage stabilization, and is to be carried out in the conditions defined by the manufacturers.

3.2 Performance Map

In order to compare the performances and benchmark the three stack technologies, performance maps will be recorded. For different targeted stack operating temperatures, the gas flowrates, stack current density, and furnace/gas preheater temperature will be adjusted by small increments in order to obtain:

- 70% steam conversion
- Thermoneutral stack operation
- Targeted stack operating temperature

Once the set of operating parameters is found, and stable operation is evidenced, a small polarization curve will be recorded around the thermoneutral current (I_{THN}, value of the current which correspond to the thermoneutral voltage of the stack, 1.3V per cell in average) at +/- 5 % of steam conversion (SC). The current ramp rate will be harmonized at +/- 1 $mA.cm^{-2}.s^{-1}$, as per SOCTESQA recommendation, and the measurements are to be recorded as follows:

$I_{THN} \rightarrow I_{THN} + 5\%\ SC \rightarrow I_{THN} - 5\%\ SC \rightarrow I_{THN}$

The different temperatures considered for the performance map are gathered in the following Table 1. The data acquired in this section will allow drawing performances curves by plotting the ASR (Area Specific Resistance) and the current density as functions of the temperature.

For each stack, the performance map will be recorded at the beginning and at the end of the protocol.

Table 1 : Temperatures considered for the performance map, according to each stack technology

700°C	750°C	770°C	800°C	830°C	850°C
CEA (CSC stack)				N.A.	
N.A.		Sunfire (ESC stack)			
3rd party stack - to be confirmed					

3.3 Durability Steps in Galvanostatic Operation

Long-term galvanostatic operation allows measuring the degradation rate of the cells. To enable direct comparison between stack technologies, despite the different nominal current densities, a two-step approach is targeted. The first step will be performed at a current density overlapping all technologies, and equal to -0.65 $A.cm^{-2}$. The second current density will be set by each stack manufacturer.

Both steps will be carried out in thermoneutral state, with a steam conversion of 70%. The temperature of the furnace and/or gas preheaters will be adjusted accordingly. Every so often, when the average cell voltage becomes higher than the thermoneutral voltage + 5 mV, the stack temperature will be increased to compensate for cell degradation and maintain the performances, up to a maximum operating temperature defined by the manufacturer. Beyond that, if the situation arises, the current will be decreased incrementally to maintain thermoneutral operation. This means, that the durability tests are quasi potentiostatic and the degradation causes a temperature increase, which will be measured inside the stack (as for the Sunfire stack). If this is not possible due to a closed air compartment (as for the CEA stack) the measurement positions must be as close as possible to the stack, e.g. the air manifolds at inlet and outlet.

For each current density, the galvanostatic operation will last 1,000 h.

The steady-state degradation will be evaluated by means of the absolute ASR degradation taking into account changes in the stack temperature. The dependency of the ASR from the temperature can be deduced from the performance map.

3.4 Load-point Cycles

This step aims at evaluation the potential impact of power ON / power OFF cycles on performances, and simulate the intermittent availability of renewable electricity. It will consist in 500 h of 5h ON, 5h OFF load cycles under constant gas flowrate (i.e. the gas composition will not be switched to safety conditions during the time at OCV or current nil), adjusted to maintain 70% SC.

The power level and current ramp rate have been harmonized at -0.5 $A.cm^{-2}$ and 5 $A.min^{-1}$. If possible, the shutdowns will be instantaneous. The transient times are included in the 5h steps.

At the end of the procedure, a steady-state step up to 500h under nominal current density, as defined by the manufacturer, will be performed to allow for possible recovery of the cell performances.

3.5 Thermal Cycles

Following the load-point cycles, two thermal cycles will be performed, between the operating temperature and 150°C. The lower limit has been chosen in order to accelerate the measurement, the last 150°C being particularly long to cool down due to the stack and furnace/hot box thermal inertia. The temperature ramp rate will be defined by each manufacturer.

Before and after each thermal cycle, the potential impact on the performance will be measured via the recording of the ASR in thermoneutral conditions at -0.5 $A.cm^{-2}$ and 70% SC for 5h. The current ramp-up will be done using the same current ramp rate as defined in the previous section.

3.6 Final Evaluation and Shut-Down Procedure

Once the different steps of the protocol have been carried out, and the final performance map has been recorded, the stack will undergo a final tightness test, as previously described in section 3.1. The stack will then be brought back to room temperature using the safety gas conditions, and the temperature ramp rate recommended by the manufacturer.

3.7 Redox Cycle

If possible, the stack will undergo a redox cycle, i.e. a cool down without safety gases, in order to simulate an uncontrolled shutdown. This will cause a partial oxidation of the Nickel in the H_2 electrode, which will be reduced after heating up the stack to operation temperatures.

4. Conclusion

This public deliverable is the first report of Work Package 2 of the EU project MULTIPLHY. It details the experimental protocol under which three stack technologies, by Sunfire, CEA, and a 3rd party commercial stack manufacturer will be benchmarked. The actual testing will take place during Task 2.2. The protocol includes initial evaluations, a conditioning step, the recording of performance maps over a range of temperatures at the start and at the end of the stack testing, a 2-step galvanostatic operation, point-load cycles as well as thermal cycles. Despite the different operating parameters of the stack technologies, the proposed harmonized protocol should enable direct comparison of performances, degradation rates, and robustness. The theoretical duration of this release test protocol is evaluated at approximately 3.5 to 4 kh.