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High Temperature Electrolysis at EIFER, main achievements at cell and stack level

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Abstract

The European Institute for Energy Research is working on the application of the solid oxide cell technology for high temperature electrolysis with the aim to produce hydrogen and syngas. Since 2004, numerous tests of single cells and stacks with 5 to 25 cells have been conducted. Test durations were rather long, ranging from 1000 to 9000 hours, with current densities between 0.4 and 1 A/cm2. A summary of the experimental results is presented with a focus on the observation of cell and stack degradation. Long term operation of cells with 45 cm2 active area under a high current density of 1 A/cm2 indicates an extrapolated cell lifetime of at least 20 000 h. Cell integration into short stacks shows additional constraints such as non-homogeneous cell behavior, electrical contacting resistances of the cell interconnects which are more critical under operation at high current density, and increased degradation rates.

Techno-economical analysis have been realized in parallel to establish the hydrogen production cost by high temperature electrolysis as function of the electrolyser environment (availability of an external heat source, electricity source, hydrogen compression stages...). Finally, the hydrogen production costs using high temperature electrolysis are discussed and the high temperature electrolysis is positioned on the roadmap of development and deployment of the electrolysis technologies for hydrogen and syngas production.

Keywords: hydrogen; high temperature electrolysis ; SOEC ; stacks

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1. Introduction

Increasing renewable power for achieving the minimum of 20% asked by the European Commission involves periods when the available power exceeds the capacity of the electric grid [1,2,3]. This excess electricity may be stored through electric devices or converted to chemical substances for seasonal storage or direct usage. Hydrogen can be produced from renewable electricity by water electrolysis and stored with low cost in underground salt caverns. The hydrogen can be used for refuelling hydrogen cars or for producing synthetic fuels (methane, liquid fuels...). This "Power-to-Gas" conversion may also be a means for creating cross-links between the different grids: electric, natural gas and heat.

This paper highlights results achieved by EIFER on the electrolysis technology working at temperatures of about 800°C. Research on this technology has started at EIFER in 2004 with the coordination of the European project Hi2H2 under financing of the FP6. Operation of circular 45 cm2 solid oxide fuel cells under high temperature steam electrolysis has been validated and 5000 h test of a short-stack demonstrated 6 to 8%/1000 h voltage degradation at -0.3 A/cm2 [4]. EIFER research activities are focussing on experimental tests aiming at characterizing the performance and lifetime of solid oxide electrolysis cells (SOEC) and stacks. Because the materials degradation under high temperature electrolysis conditions is not linear, the interest is to operate cells and stacks longer than 1000 h. A 9000 h of high temperature electrolysis test was realized on a single cell from the Forschungszentrum Jülich [5].

In the frame of the European project RelHy [6] (EU research program FP6), short-stacks, 5 to 10-cell stacks from the company Topsoe Fuel Cell were operated during more than 4000 hours [7]. Finally, a 25-cell stack was operated continuously in the electrolysis mode for more than 2900 h. The objective of these long term test is the identification of mechanisms responsible for degradation of cells and stacks performance. Finally the efficiency and economy of producing hydrogen by high temperature electrolysis is analyzed in the different uses of hydrogen.

2. Experimental

Experiments are carried out in order to examine the degradation and the longevity of high temperature operating materials initially developed for Solid Oxide Fuel Cells (SOFC) under the high temperature electrolysis conditions. These tests have increased in scale from single cells through 5 and 10-cell stacks, and most recently to the testing of 25-cell stack. Performance and lifetime of different oxygen electrode materials and cell designs (e.g. electrode-supported, electrolyte supported) have been evaluated through single cells tests. Results of single cell and stack tests have been documented in several papers [8,9,10,11,12,13]. The measurements were carried out in SOFC test benches from ECN (The Netherlands) and from the society FuelCon (Germany), adapted at EIFER for high temperature electrolysis operation (cf. Figure 1). For single cells tests, the cell was placed in an unsealed alumina housing with current collectors made of platinum (SOEC anode) and nickel (SOEC cathode) double grids and a Pt backbone wiring placed between grids and housing. In this configuration the hydrogen in the outlet gas is burnt at the rim of the cell. Thermocouples measured the temperature in the centre of the cell. Cell voltage was measured with Pt sense wires welded to the grids close to the rim of the cell. Stacks from Topsoe Fuel Cell were mounted in a test rig as shown in Figure 1 (left) under a compression force of 200 - 500 kg. The stack, developed for fuel cell operation, is based on the so-called Alpha design. It integrates 5 to 25 planar SOFC anode supported cells of 100 cm2 active area.
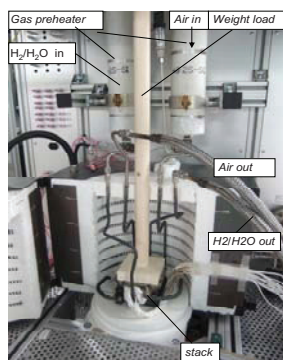
Figure 1: Photo of the 25-cells stack mounted inside the oven of the test bench.

Cells tested are Ni-YSZ hydrogen electrode supported cells with YSZ (yttria doped zirconia) electrolyte and either LSM (strontium-doped-lanthanum manganite) or LSCF (strontium-doped lanthanum cobaltite ferrite) oxygen electrodes [14,15]. The cells are sandwiched between protected (coated) Crofer interconnects. The feed gas to the oxygen electrode was air. A mixture of 80 to 90 vol.% of steam in hydrogen was supplied to the hydrogen electrode. The steam was generated from high purity water with controlled evaporation mixing unit (CEMs) heated to above 100 °C, as all the upstream tubing, or by optimised commercial evaporators (FuelCon).

3. Results

Circular anode-supported SOFCs from Forschungszentrum Jülich with an active cell area of 45 cm2 were galvanostatically operated under high temperature electrolysis at j = -1 A/cm2. Electrolytes consisted of a dense layer of 8 mol% yttria-stabilised zirconia (8YSZ). The oxygen electrode was made of LSCF with a thickness of 35-40 µm, and the steam/hydrogen electrode was a Ni/YSZ cermet (8 µm thickness) on a 1.5 mm thick Ni/YSZ supporting substrate. The test duration of this was the longest reported in the literature with 9300 h of operation, of which 9000 h were at j = -1 A/cm2 (Figure 2 taken from ref. [5]).
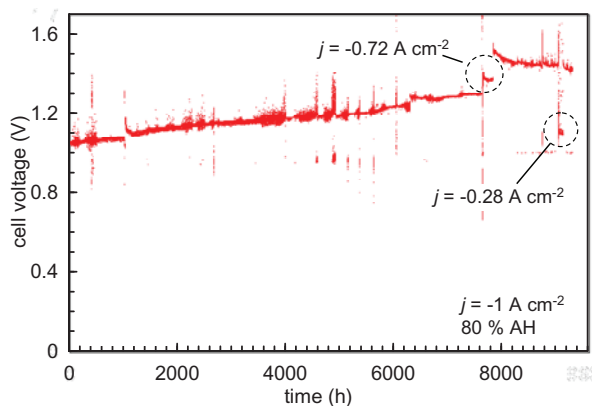

Figure 2: Time evolution of the cell voltage during operation with a nominal j= -1 A/cm2.

Voltage degradation over the entire experiment was 3.8 % (40 mV)/kh (**Error! Reference source not found.**). Several experimental incidents have contributed to the degradation [5]. During the middle period of the experiment of the LSCF based cell, from 2000 to 5600 h (cf. Figure 2) which was free of major incidents, only 1.7%/1000 h (19 mV)/kh degradation was measured. Under these operation conditions, voltage degradation is the lowest reported in the literature. A high Faradaic efficiency was maintained for the cell voltages covered in the experiment. Combined with the low cell voltages an electrical-to-chemical energy-conversion efficiency of more than 100 % was achieved during most of the experimental time. With an OCV of about 0.85 V at 800 °C, about 0.45 V voltage losses (Uthermal neutral = 1.3V – OCV) are tolerable due to current flow and degradation. If, moreover, no external heat source is available for evaporation, the voltage can further rise to Ucell = 1.48 V (the ΔH/e value at ambient temperature [16,17] and the heat from the now exothermal reaction is used for evaporation [8]. These consideration lead to a relatively wide Ucell range and correspondingly long operation times of 25000 hours as shown in the Figure 3. With the LSCF oxygen electrode it is assumed that (i) operation starts endothermally with Ucell = 1.06 V (taken from the **Error! Reference source not found.**), and (ii) operation is continued until the heat generation equals the initial heat consumption, i.e. up to Ucell = 1.54 V. Such final voltage still means a largely reduced thermal load to the cell compared to SOFC operation. Smaller |j| values would further widen the operation window via a lower initial Ucell and also via a lower degradation rate, since degradation commonly rises with increasing current density. Under such conditions the cell approaches the requirements for practical application.
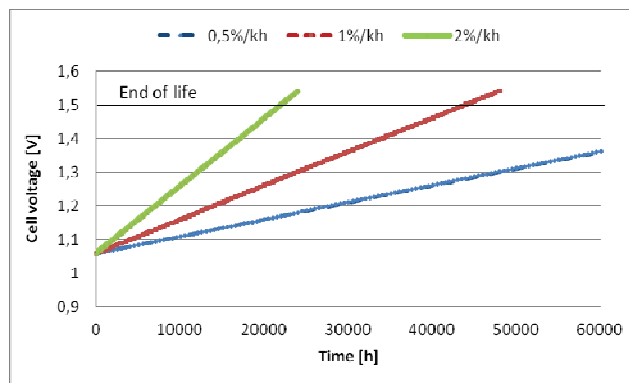

Figure 3: Calculated evolution of the operation cell voltage for different degradation rates in % of the initial cell voltage (1.06 V) per 1000 h.

Impedance spectroscopic measurements done during the 9300h of experiment show that at least two degradation processes contribute to cell degradation: (i) an increase in ohmic resistance attributed to the electrolyte resistance Rion(YSZ), and (ii) a non-ohmic contribution due to electrode degradation. The first process seems to be specific for SOEC operation, with a Rion (YSZ) increase higher than in the SOFC mode. Significant electrolyte degradation implies that the contribution of anode and cathode deactivation to degradation remains moderate, possibly with rates not far above the ones in the SOFC mode.

When operating a short-stack additional constraints apply and additional degradation occurs. Long term tests of 5 to 10-cells stacks from the company Topsoe Fuel Cell, tested in the frame of the European project RelHy, are summarized in the

Table 1. This table gives the evolution of EIFER high temperature electrolysis test facilities from 5-cell to 25-cells between 2009 and 2012.

Table 1: Overview of stacks tests

Date	Stack type (No)	Cells	SOEC operation time (h)	Current density (A/cm^2)	Steam conversion	Degradation rate (%/kh)**
2009 [11]	5-cell (I)	LSM CSC[a]	2651	-0.4 / -0.6	39 - 58%	~3 %
2009 [12]	5-cell (II)	LSCF ESC[b]	4050	-0.4	39%	~5 %
2010	5-cell (III)	LSM CSC[c]	1250*	-0.8	52 %	~4 %
2010	5-cell (IV)	LSM CSC[a]	2000*	-1.0	52 %	~5 %
2012	25-cell	LSM CSC[c]	1056*	-0.8	56 %	ongoing

[a] Cells made by DTU-Risoe (Denmark), [b] Cells made by ECN (The Netherlands), [c] Cells made by Topsoe Fuel Cell (Denmark), *at the given current density, **temperatures increase with time (oven temperature adjusted only at stack III).

In 2010, a repetition of the first 5-cell stack tests (I and II) [11,12] done within the RelHy project was done, using again cells with LSM oxygen electrodes but with improved endplate contacting. High voltage drops at the endplates had complicated the first two test runs. Sense wires were welded to the endplates to measure continuously the voltage drops at the endplate contacts. A drastic lowering by one order of magnitude to below 0.1 V as well as a stabilisation was achieved for the voltage of the positive endplate at the stack bottom. Also the voltage of the negative endplate decreased slightly to below 0.2 V. The contribution of such endplate voltage drops only causes minor heating of the adjacent cells, and does not perturbate significantly the thermal conditions for stack operation.

The stack (III) operated 2160 h under high temperature electrolysis. After 340 h operation under j = -0.4 A/cm2, the current density was changed to j = -0.8 A/cm2 value and the stack continuously operated during 1070 h under this current density. Without counting the serial repeating unit 1 (SRU 1), the average SRU voltage stays below the thermal neutral voltage during the entire 1070 h operation period under j = -0.8 A/cm2 and an average endplate temperature below 820°C. Stack-voltage degradation of stack (III) over the 1070 h period under j = -0.8 A/cm2 is rather linear and amounts to 3.7 % / 1000 h (equivalent to 46 mV / 1000 h voltage increase per serial repeating unit, SRU).

The stack (IV) was operated during more than 2400 h, initially during 334 h under j = -0.5 A/cm2, then during 20 h under j = -0.8 A/cm2, and finally during 2000 h under j = -1 A/cm2. An important result is the essentially stable voltage of the stack (IV) from about 900 h until the end of the test (Figure 4).
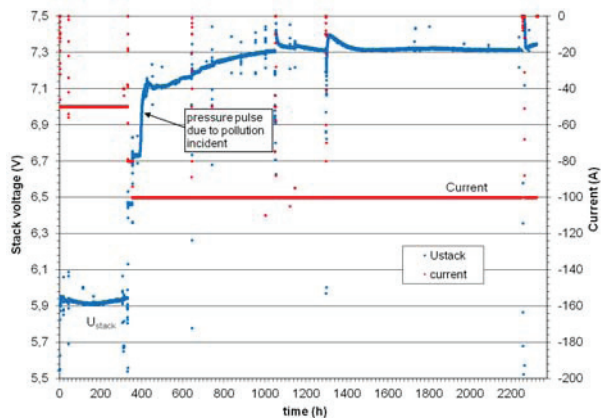
Figure 4: Time evolution of the current and the stack voltage at the 5-cell stack IV.

At the starting of the experiment at a current density of -0.5 A/cm2, the SRUs behaviour was inhomogeneous with voltages varying from 1.12 to 1.28 V as shown in the Figure 5. An increase of the current density to -1 A/cm2 led to a stack voltage slightly above 6.7 V with all SRU voltages above the thermal neutral voltage. At 395 h a pressure pulse caused by a partial blocking of the humidification system was observed which led to a strong increase of the stack voltage (+ 360 mV) and corresponding temperature rise. Pollution from the water supply (tubing) is thought to be responsible for the electrode deactivation in the stack. As consequence, following almost zero-degradation period at 900h can be understood as either a degradation decreasing strongly with time, or as the result of cell reactivation (after the pollution incident) compensating degradation. Stack operation during this period was exothermal with about 90 W thermal power from the SRUs, and further contributions from the endplate-to-cell contacting (~30 W) and the contacting to the current rods. The heat release from the SRUs is comparable to the one under SOFC operation with an around 5 times lower |j| value. So, thermal conditions similar to those under SOFC operation could be a simple explanation for SRUs voltage stabilisation.
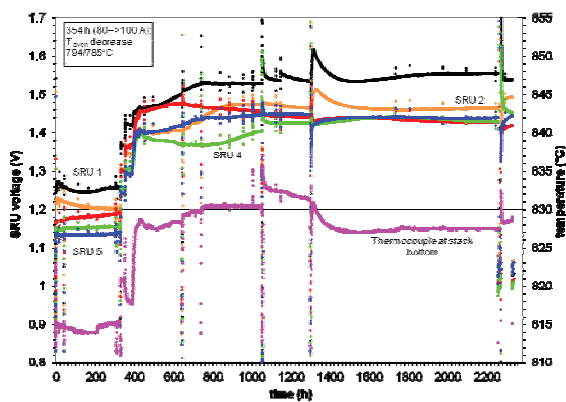

Figure 5: Time evolution of the SRU voltages and endplate temperatures at the 5-cell stack (IV) (SRU 1 at stack bottom; oven
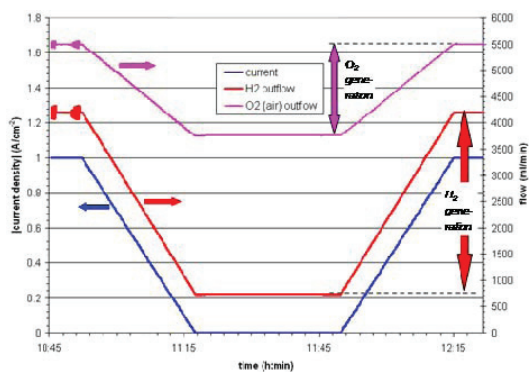

Figure 6: Variation of the gas outflows as function of the current at the 5-cell stack IV after 645 h SOEC operation.

temperature is 782°C at t > 1300 h).

The hydrogen outflow is linear in the current, as shown during SOEC operation of stack (IV) in Figure 6. The generated hydrogen flow of 2.77 Nl/min represents 100 % of the calculated value from the Faraday law, which means ideal current efficiency.

The capital cost of the technology and the economics of operation are major factors in determining the efficiency and long-term perspectives for the different electrolytic processes. High temperature electrolysis of steam (HTE) is expected to consume less electrical energy as compared to electrolysis at low temperature as consequence of the more favourable thermodynamic and electrochemical kinetic conditions for the reaction [8]. The hydrogen production cost by HTE has been reported in several works where the electrolyser is coupled with various high temperature sources [18,19,20,21,22,23]. The hydrogen production capacity of the electrolyser plant chosen in this study is 5 tons per day which correspond to 208 kg/h of hydrogen considering a production all day long. Based on the high heating value (HHV) of hydrogen, this corresponds to 8210 kWH2 equivalent power. Considering that the high temperature electrolyser operates at the thermal neutral voltage (1.29 V at 800°C), the corresponding electrical power, Pelec, required to achieve this production is 7130 kWe. Electrical consumption of the inverter needs to be added to Pelec. The conversion efficiency of the inverter is fixed to 95% which led to 7505 kWe. From the target mass production the molar stream flows were determined. To avoid partial oxidation of the hydrogen electrode as well as a tubing corrosion, the cathodic feed stream of the electrolyser contains 10 vol.% of hydrogen coming from a recycling loop from the produced hydrogen. The actual electrolyser hydrogen production is therefore not equal to 5 tons/day but 5.8 tons/day. For system convenience the electrolyser operates at a pressure of 1.3 bars, without pressure drop. It enables to use fewer components (compressors and heat exchangers) all together with keeping the stream pressure always above 1 bar. Hydrogen produced is then compressed to 300 bars (conventional pressure for metal cylinder storage). Characteristics of the model electrolyser are summed-up in

Table 2.

Table 2 : Model electrolyser characteristics

Hydrogen Production [kg/h]	208	Operating pressure [bar]	1.3
Cell voltage [V]	1.3	Pressure drop [bar]	0
Electrolysis efficiency at the stack level (theoretical value 1.48V at ambient temperature) [%]	115	Inlet mix flow (H2O + H2)in [kg/h]	2660 H2O +33 H2
Power [kW]	7130	H2O-to-H2 conversion ratio [%]	70
Electrolyser + inverter input power [kW]	7505	Outlet mix flow (H2O + H2)out [kg/h]	798 H2O +241 H2
Operating mode	Thermal neutral (1.29V at 800°C)	Outlet oxygen flow [kg/h]	1653
Operating temperature [°C]	800		

The cost of hydrogen (€/kg) is calculated the following way:

$$\text{Cost}_{H_2}\left(\frac{\text{€}}{\text{kg}}\right) = \frac{\sum_{n_{year}=1}^{21} (\text{Exploitation cost}_{n_{year}}\,(\text{€}) + \text{Investment cost}_{n_{year}}\,(\text{€}))}{\text{Total production (kg)}} \qquad (1)$$

It corresponds to the sum over 21 years of yearly costs, including exploitation costs and investments cost. Hypotheses are done on material investments life-time, enabling to know each year which part of the system has to be replaced. The cost calculation considers one year of construction (nyear = 1) and 20 years of operation. A value of 8 % was used for the annual discount rate.

Table 3 : Hypothesis of the techno-economic analysis

Element	Unit cost	Lifetime (hours)
SOEC stack lifetime before refurbishment [24]	200€/kWe – 2000€/kWe	20 000 - 40 000
Inverter [25]	50 €/kWe	87 600
Compressors [26]	700 €/kWe	50 000
Heaters (ref. Manufacturer INDEECO (U.S.A))	70 €/kW	50 000
Heat exchanger [24]	20% of stack investment	20 000
Separators, mixers & pump	1.5€/kW	50 000
Electricity	0.03 €/kWh - 0.10 €/kWh	-
Pure water	1.5 €/m³	-
Cooling water	0.5 €/m³	-
Maintenance [26]	4% of electrolyser price	-
Discount rate	8%	

   It was found that the cost of the high temperature electrolyser's balance of plant represents about 2/3 of the investment of the electrolyser. The hydrogen production cost is mostly influenced by the electricity price as shown in the Figure . For example part of the hydrogen production cost related to the price of electricity represents 69% and 84% respectively for a 20 000h and 40 000h lifetime SOEC of 1.2 MWe operating 100% of the year with an electricity price of 50 €/MWe.
   Other parameters influencing the hydrogen production cost are firstly the capacity of production of the electrolyser and, secondly its time of operation in hours over the year. With an electricity price of 50

€/MWe the hydrogen production cost varies between 2.45 and 3.45 €/kg when operating electrolysers of H2 production capacities between respectively 50 and 900 Nm3/h H2 during 4360 or 8760 hours per year. Dividing the SOEC lifetime by two (20 000 hours) increase the hydrogen production cost to 2.64 and 3.65 €/kg.
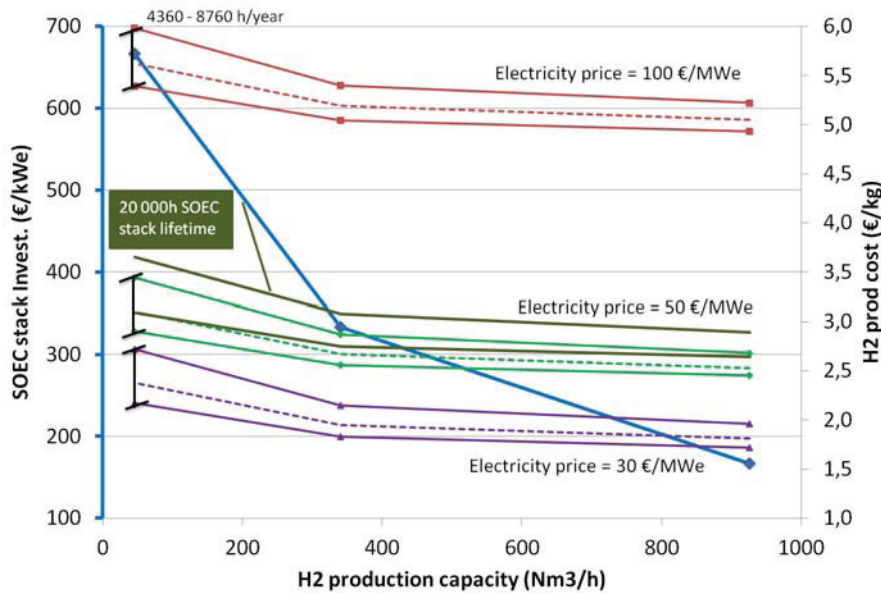

Figure 8: Hydrogen production cost with high temperature electrolysis as function of the SOEC stack investment, the H2 production capacity (Nm3/h) of the electrolyser, the electricity price and its time of operation per year.

The hydrogen production cost with high temperature electrolysis is particularly interesting when electricity price is close or below 50 €/MWe. With this electricity price the hydrogen production cost is in the close and even lower than the cost obtained with alkaline electrolysers (~3.5 €/kg for large H2 capacity of electrolysers).

4. Conclusions

EIFER has tested number of cells from industrial and research partners achieving more than 9000 hours operation at -1 A/cm2 and a final degradation of 3.8%/1000 h. The degradation was 1.7%/1000 hours between 2000 and 5600h which was free of incidents. A similar degradation of 3.7%/1000 h was measured with the third short-stack (-cells) operated at -0.8 A/cm2 during 1070h. A stabilization of the degradation was observed when operating the short-stack exothermally (stack IV). Indeed, heat production in the stack seems to be favourable for stabilizing the resistance of serial repeating units with expected better electric contact between the cells and the interconnects. This trend may be explained by the design of the stack previously made for solid oxide fuel cell operation and which is not adapted for the endothermal reaction of steam electrolysis. Finally, the hydrogen production cost calculated as function of the electricity price and the electrolyser hydrogen production capacity varies between 2.45 and 3.45 €/kg (electricity price of 50€/MWe) when the SOEC lifetime is 40 000 hours (1%/1000h degradation). Decreasing the lifetime by a factor two increases the hydrogen production cost to 2.64 and 3.65 €/kg.

Consequently research is still needed to understand and reduce the degradation at the cell level and develop dedicated SOEC stacks.

Acknowledgements

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