

RelHy Final Report

Executive summary

The RelHy project targeted the development of novel or improved, low cost materials (and the associated manufacturing process) for their integration in efficient and durable components for the next generation of electrolyzers based on Solid Oxide Electrolysis Cells (SOEC). It was specifically tailored for i) optimisation of novel or improved cell, interconnect and sealing materials and ii) achievement of innovative designs for SOE stacks to improve durability.

The main challenges addressed were the simultaneous achievement of both, lifetime (degradation close to 1% for 1000 h on single repeat units at 800°C) and efficiency (0.03 to 0.04 gH₂/cm²/h, i.e. approximately 1 A/cm² with water utilisation >60%). These operation points and degradation values yield an efficiency of up to 80% (LHV) at the system level with >99% availability. Cost issues have also been addressed by considering cost effective materials and processes in order to meet the “non energy” 1€/kg H₂ target.

The RelHy project has allowed successful material improvement: Two types of cells have been studied. With O₂ electrode made of LSCF/CGO, cathode supported cells exhibited very high cell performances. Their degradation rate was found to be promising as a stabilisation plateau (around 1% per 1000h) was obtained after few 100 hours at intermediate current densities. Electrolyte supported cells with 3YSZ electrolyte showed greatest durability whereas with 10Sc1CeSZ electrolyte high performances were reached.

Protective and contact coating made of Co₂MnO₄ spinel deposited on Crofer by PVD and of screen-printed LSM showed stable ASR at 800°C in ex situ testing and in operation.

Several glass seals, either commercial or homemade, were shown to withstand electrolysis conditions and to ensure tightness for more than 4000h.

Thanks to simulation, it was shown that in stack configurations, with limited heat dissipation, significant thermal gradient can occur across cells and upon transient temperature excursions are unavoidable.

Two tests campaigns have been achieved with SRUs and short stacks including performances and long duration tests (4000h) on reference and improved components. Some conditions could be found with no degradation, and high current densities at degradation rates < 5% per 1000h were reached in SRU and short stack. Scaling up to 25-cell stack has been achieved highlighting issues specific to electrolysis operation.

Description of the project context and main objectives

In the perspective of increasing energy demand, exhaustion of fossil energy sources and the green house effect causing climate perturbations, a major interest in renewable, hydrogen oriented economy and CO₂ neutral energy production has appeared worldwide. In this context, High Temperature Electrolysis (HTE), based on reversed solid oxide fuel cell technology, applying in particular electricity produced from renewable sources, appeared as a promising CO₂ free hydrogen production method.

This technology is not new; Dornier in the 80s had already developed a tubular ceramic SOEC prototype producing 1Nm³/hr of H₂ at 1000°C (Project Hot Elly) that had been operated for more than 500h with an electrochemical conversion efficiency of ~ 100% LHV significantly better than that classically obtained with current alkaline electrolyzers ~65% LHV. However, due to the high cost of the electrolyser and to the absence of short-term industrial application this work has ceased.

In the 2000s, new motivations appeared to promote the development of high efficiency hydrogen production means and several economical studies either internal (at CEA, ECN or EIFER) or published have highlighted the economic interest of HTE for hydrogen production. Owing to the significant progress achieved in the Solid Oxide Fuel Cell technology during the last 25 years, all newly involved actors developed planar Solid Oxide Electrolyser (SOE) prototypes with materials and designs that directly derive from SOFC technology. The RelHy project was built on the Hi2H₂ project results and more specifically on the issues highlighted in this project regarding the operation of SOFC component in the elect(rol)ysis mode. These issues were related to a degradation rate particularly high at high current density and in stack environment. The project was structure to take advantage of material reasearch under progress in the on going SOFC projects REAL-SOFC and SOFC600, as such it was positioned as a bridge between current good performing electrolysis cells and their efficient and reliable integration into advanced stacks to pave the way for the production of a new generation of electrolyzers.

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It was specifically tailored for i) optimisation of novel or improved cell, interconnect and sealing materials and ii) achievement of innovative designs for SOE stacks to improve durability.

The expected final results were the simultaneous achievement of both, lifetime (degradation close to 1% for 1000 h on single repeat units at 800°C) and efficiency (0.03 to 0.04 gH₂/cm²/hr, i.e. approximately 1 A/cm² with water utilisation >60% and a stack efficiency > 90%). These operation points and degradation values would yield an efficiency of up to 80% (LHV) at the system level with >99% availability. Cost issues was also to be addressed by considering cost effective materials and processes in order to meet the “non-energy” 1€/kg H₂ target.

To achieve these goals, the RelHy project was based on the coupled development of instrumented single repeating units (SRUs) and short stacks and of associated simulation tools (from cell to stack scale). Since the project is centered on R&D activities, the RelHy multidisciplinary European consortium was merging expertise from two university laboratories and three research centres already recognised for material development and cell production, instrumentation and testing, and modelling (DTU-Risoe, Imperial College, ECN, EIFER and CEA) and also from a fuel cell stack manufacturer that can produce electrolyser stacks (TOFC) and from an energy company (HELION) that can specify the operation conditions and assess the competitiveness of the innovative electrolyser prototype and its potential integration.

Description of the main S&T results

In order to optimise current available materials, the RelHy project has started with the fabrication of a first batch of materials, representative of the current state of the art, to be tested in the electrolyser mode as reference materials. These materials have been chosen in agreement with the results of the previous Hi₂H₂ and Real-SOFC projects as well as with the on-going SOFC600 one. The first batches of reference cells were composed of:

- Cathode supported cells (CSC): Ni-YSZ/8YSZ/LSM-YSZ fabricated at DTU-Risoe
- Electrolyte supported cells (ESC): Ni-CGO/3YSZ /LSCF fabricated at ECN
- CROFER had been selected as the reference interconnects material, LSM as the reference coating at the anode side and NiO at the cathode side.
- A reference glass seal was selected and used in the form of pre-sintered glass bars for purpose of reproducibility between testing laboratories

In parallel first cell material developments and optimisation have been achieved to adapt these materials for the SOEC application. A particular focus was given to:

- Protection of Ni-Cermet cathode against Si poisoning;

- Fabrication of electrolyte supported SOEC with 10CeScZrO_2 to ensure higher ionic conductivity while keeping thin hydrogen electrode submitted to high steam content;
- For performance and durability issues, major attention was given to the development and optimization of combinations of interconnect and contact and/or protective coating;
- To improve the seal durability, several glasses having a softening point consistent with the operating temperature and able to resist thermal cycling have been tested and compared;

During the first year of the project a Common protocol covering all aspects of cell, SRU and stack testing, including the methodology for characterisation of cell performance and degradation has been created in conjunction with all testing partners. With the completion of the test protocol, it was the aim of the project to disseminate it publicly such that it would be used by institutes outside of RelHy. In this manner, it was hoped that the RelHy protocol would be adopted as a common protocol (or becomes the basis of) for SOEC testing, at least within the EU.

- **Heating, Sealing and Ni reduction** following cell manufacturer recommendations
- **Test start-up**
 - OCV stabilisation at 800°C under H_2 with 3 vol.% H_2O
- **Operation in fuel cell mode at 800°C to check SRU performance**
 - EIS at OCV, j-V curves and $\text{EIS} = f(j)$
- **Operation in Electrolysis Mode at 800°C :**
 - Change of humidity **50 vol.% Hum** (H_2 10%/N₂ 40%) and stabilisation at OCV,
 - EIS at OCV, j-V curves $V \leq 1.5\text{V}$, $\text{EIS} = f(j)$,
 - Change of humidity **70 vol.% Hum** (H_2 10%/N₂ 40%) and stabilisation at OCV,
 - EIS at OCV, j-V curves $V \leq 1.5\text{V}$, $\text{EIS} = f(j)$,
 - Change of humidity **90 vol.% Hum** (H_2 10%/N₂ 40%) and stabilisation at OCV,
 - EIS at OCV, j-V curves $V \leq 1.5\text{V}$, $\text{EIS} = f(j)$,
 - Back to **50 vol.% Hum** to change operation temperature to 750°C
- **Operation in Electrolysis Mode at 750°C**
- **Operation in Electrolysis Mode at 850°C :**
- **Durability test at 800°C (-1 A/cm^2 under 90 vol.% Hum/10 vol.% H_2)**

Relhy test protocol

To assess the economic pertinence of High Temperature Steam Electrolysis (HTSE) for hydrogen production and more specifically of the technology considered here, specifications for industrial electrolyzers interfaced with either nuclear power plant or with renewable energy (wind turbine) have been identified and analysed. The approach has consisted in transforming the hydrogen production cost (expressed as costs for installation, for operation, for maintenance and for end of life options) into cell operating conditions (operating temperature and pressure, level of cell performance at a nominal operating point, durability and robustness upon load transient) and cell

characteristics (active area, steam utilisation, etc.). This has given a complete set of HTSE properties from the end user point of view, to be iterated with the component development team.

This analysis showed that basically the same specifications could be used at this stage of the development of the technology and has confirmed that the current targets of the RelHy project established a good step forwards to reach economic relevance.

	RelHy Targets	Nuclear		Wind	
		Short	Medium	Short	Medium
Degradation ($\mu\text{V/h}$)	15 $\mu\text{V/h}$ ~1%/1000h	10 0,7%/1000hrs at 1.5V	5 1%/1000hrs at 1.5V	15	5
Lifetime (hrs)	Tests 1000 to 5000 h	10 000	20 000	16 000	40 000
Thermal cycles/year		2	5	7	14
Voltage/cell (V)	< 1.5V	<1.5	<1.5	<1.5	<1.5
Current (A/cm^2)	1 A/cm^2	1.5	2.0	1.0	1.5
Pressure max (bar)	1 bar	50	50	20	30
Active Area (cm^2)	~100 cm^2	400	800	300	600
Start up from 600 C		< 4 h	< 4h	< 2	< 1h
Turn down to 20 %		?	?	< 2 min.	< 30 sec.

Relhy targets versus industrial specifications for electrolysis plant coupled with a nuclear reactor or a wind turbine.

The second year of the project was focused on the evaluation of potential second generation SOEC stack components in order to meet the lifetime and efficiency targets:

- For single cells, either with improved electrolyte supported cells (ESC - Ni-CGO/ScSZ//LSCF) or with improved cathode supported cells (CSC - Ni-YSZ/8YSZ//LSCF) it has been possible to reach -1 A cm^{-2} below 1,5 V. Degradation rates of reference (3YSZ electrolyte) and improved ESC were equal or lower than 2% per 1000h at the cell level whereas they were higher for CSC. Initial analysis of degradation mechanisms indicated cracks and delamination of the electrolyte, Ni coarsening at the cathode side and also significant contribution from the anode side.
- LSM and LSCF coatings screen printed on Crofer plates showed stable ASR $<0,05 \text{ } \Omega\text{cm}^2$ in air for 1000h. When integrated in an unsealed SRU, they were efficient contact coatings, but did not prevent long term oxide layer growth and some Cr reactivity with LSCF.
- Several glass seals and Thermiculite seal exhibited satisfactory compatibility with Ni-Cermets and Crofer interconnect materials upon 1000h ageing in steam environment and showed leak rates below 0.5% of the anode/cathode flow at a pressure difference of 20 mbar.

Several innovative individual materials and components appeared most promising for HTSE application.

State of the art materials have been integrated in SRUs and short stacks and tested according to RelHy testing protocol. Good and similar initial performances were obtained by all partners in SRUs and in short stacks. However, in all SRU tests severe degradation rates were obtained (>20 % per 1000 hrs), associated to increasing gas leakage and ASRs. Significant discrepancies between SRU tests results were attributed to poor reproducibility of cell and interconnect electrical contact. In all cases ageing was started with exothermic cell voltages where the degradation aggravated exothermic mode.

In the short stacks, the inner cells, either CSC or ESC, showed reproducible and satisfactory behaviour and experience low degradation (3% per 1000h at 0.6 A cm^{-2} for CSCs). Only limited leakage was detected and for both stacks the inner cells ageing commenced in the endothermic mode.

These results were aligned with the HTSE road-map established on the basis of industrial specifications.

Microstructure simulation results showed the effect of particle and pore former initial size and of sintering extent on expected cathode current density, giving indication for further component improvements. 3D-stationary macro-modelling allows simulating nominal SRU operation and confirms the origins of losses in cell performance. 1D-transient simulation complements the 3D approach allowing estimates of a given cell behaviour in a stack upon transient. This mixed approach opened the door to control strategy analysis.

Since some discrepancy between test results had highlighted the influence of operation parameters such as electrical contacts within the cell, load homogeneity or tightness, in the third year a focus was given on the control of these parameters and on the reproducibility of the experimental results. Improved electrolyte supported cells (Ni / Ni-GDC / GDC / 110 μm thick 10Sc1CeSZ / YDC / LSCF) were developed and evaluated in single cell tests. They fulfilled RelHy performance and durability targets. However, they happened to be too brittle to be chosen for final prototype. Improved cathode supported cells (Ni-YSZ / YSZ / CGO / LSCF-CGO) were also tested, exhibiting high performance level (-1 A.cm^{-2} at 1.25V) and lower degradation rate when tested in single cell set up that state of the art cells although not entirely fulfilling the RelHy target. They have been selected for the final 25-cells prototype.

Micro modelling has allowed determining optimal cathode microstructure (in terms on length of TPB, Ni and YSZ particles sizes and pore size and ratio). This work has opened the door for some comparison between real microstructures, measured exchange current densities and effective transport properties and simulated ones.

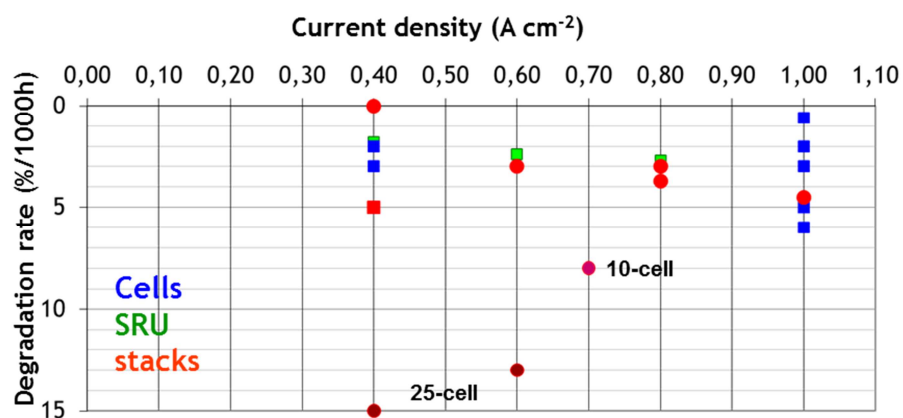
A second generation SRU has been developed, based on recommendations coming from macro-modelling and sensibility analysis done on SRU design. It integrated improved control of the plate

flatness, modified tightness design and protective coating under the contact coating. With this 2G SRU, satisfactory reproducibility was obtained and degradation rates as low as 2% per 1000h at -0.4 A cm^{-2} was obtained for state of the art electrolyte supported cell in good agreement with short stack results. Long duration tests have been run on two additional 5-cells short stacks provided by TOFC with improved endplates contact coatings and tightness, integrating state of the art cathode supported cells. Satisfactory voltage between endplates was measured, more homogeneous behaviour among the 5 cells was obtained and low degradation rates (between 3 to 5 % per 1000h) have been demonstrated between -0.4 to -1 A.cm^{-2} . On the basis of these results operation conditions for final prototype have been defined.

In the last year of the project material optimisation and processing task was finalised. In particular the characterisation of interaction between sealants hydrogen electrode or interconnect were finished allowing to select most promising seal. The understanding of 2G-CSC degradation mechanisms was pursued, and batches of 2G-CSC were fabricated for stack testing.

One last 2G-SRU was fabricated integrating a reference CSC for testing. One 10-cell stack was fabricated and tested to allow a progressing scaling up between 5-cell short stacks and 25-cell final stack prototype. Then the 25-cell final stack prototype was be fabricated and operated. Owing to unexpected experimental behaviour, including sudden voltage increase or decrease, a second one was also fabricated and operated that was found to reproduce similar behaviour.

All these SRU and stacks were tested and had their behaviour analysed. In general a promising behaviour was reached, with limited degradation rate (in the range of few % per thousand hours and below 5 % per thousand hours) up to high current densities (1 A cm^{-2}) with cell voltage below 1.5V. Upon scaling up some voltage instabilities were found and tentatively associated with contact modifications under endothermic operation resulting in high “average” voltage degradation rate.



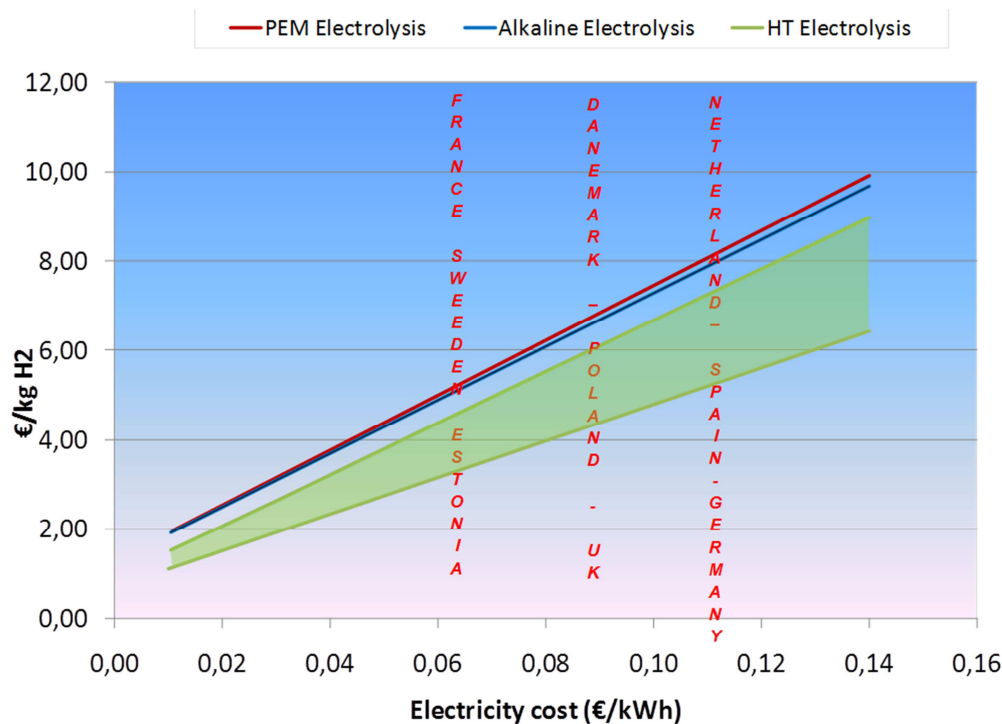
Voltage degradation rates measured in the Relhy conditions with single cells, single repeating units and stack operated in electrolysis mode at specified current density

Nevertheless, some conditions could be found even with the stacks with limited degradation and stable electrolysis operation. As such the project technical targets were considered to be reached.

Micro modelling was further validated and some extension to calculate effective conductivity, exchange current density, and diffusion coefficient of real cathode structure reconstituted using 3D tomography were done.

The analysis of SRU design and the identification of solutions for improving its efficiency were finalized using macro modelling. This work encompassed a specific analysis of the influence of acceptable pressure drops along the channels and an evaluation of the effect of electrical conductivity variations, potentially linked to anode cracking upon mounting, on the global SRU behaviour.

The competitiveness assessment of high temperature steam electrolysis finished the project. Based on the results obtained in the project, a cost analysis and an environmental impact analysis of the hydrogen produced by a High Temperature Steam Electrolyser were done.



The competitiveness of HTSE was established.

Description of the potential impact

The main targets of the RelHy project have been reached (adaptation and integration of cost effective cell, interconnect, coating and sealing materials in efficient and durable solid oxide electrolyser components and construction and testing of a laboratory prototype electrolyser integrating these innovative materials and stack designs). As such, the Relhy project has paved the way to low cost and low carbon footprint hydrogen production.

However, in economically relevant operation conditions, in other words at high current densities (and high hydrogen production rate), degradation rates obtained in the project remained higher than initially targeted. Main causes of solid oxide electrolyser degradation have been proposed by the consortium mainly linked to ohmic resistance increase with time that would come essentially from interfaces degradation and from material destabilisation (electrolyte, electrodes, contact and protective layers).

To overcome these degradation mechanisms, R&D efforts should be concentrated in the development of materials with composition and microstructure tailored for high temperature electrolysis operation in order to exhibit higher material stability under high steam contents, higher interface robustness, gas evolution and species transport properties compatible with porosity gradient, etc.

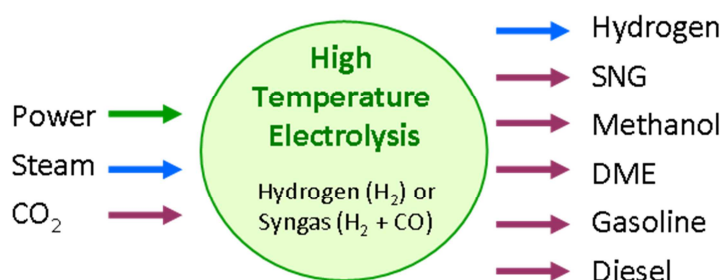
Thermal management of high temperature electrolyser stacks also appeared to be a key issue. As a consequence, system integration should also deserve particular attention, especially the steam production unit and the thermal management, both being liable to increase drastically the electrolyser lifetime.

To open further the potential impact of the RelHy project and its societal implication, the assessed competitiveness of the technology has allowed identifying some market opportunities of high temperature electrolysis and associated technical requirements, (some of them being already reached in the RelHy project). They seem reachable within medium term future and are summarized hereafter:

- Each solid oxide cell should be run close to thermo-neutral voltage
- Solid oxide cell temperature should range between 700 - 800°C
- At the cell level a steam conversion rate between 60 to 80% should be targeted
- Stack lifetime should be at least 2 years

- Accordingly, the voltage degradation rate should be lower than 2% per 1000h and even in the medium term, lower than 1% per 1000h
- To improve the complete system integration and efficiency, the next step is to consider operation under pressure (5-50 bars) in order to avoid the first pressurisation step of hydrogen.

Workshops organised within the frame of the RelHy project also allowed to extend the market opportunities of high temperature electrolysis (HTE). Indeed, HTE is a key enabler technology in future energy scenarios with large share of low carbon energy sources such as renewables or nuclear. It allows producing hydrogen from steam with low carbon footprint. Fed with steam and CO₂ mixtures it allows producing syngas by co-electrolysis constituting a CO₂ valorisation path. Both hydrogen and syngas constitute storable and valuable energy vectors. Moreover, syngas can be further converted into synthetic natural gas (SNG) or various liquid hydrocarbon, allowing countries to lower their energy dependency.



- With electricity coming from intermittent energy sources, HTE enables intermittent renewable energy storage and production/consumption peak shaving.
- Because it can take advantage of available heat, HTE offers higher electrical efficiency than other commercial electrolysis technologies, close to 100% (compared with current alkaline technology with electrical efficiency around 55-75%)
- Several markets for HTE technology exist in current industrial processes. Current state of the technology already allows addressing niche markets such as biomass gasification intensification or SNG production. HTE large scale commercialization seems achievable in 2020.