Hydrogen from Regenerative Energy Power Sources: pressurised alkaline electrolyser with high efficiency and wide operating range

The Project „RESelyser“

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The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n° [278732] 10

1 DLR Deutsches Zentrum für Luft- und Raumfahrt e.V. in der Helmholtz-Gemeinschaft
2 vito vision on technology
3 HYDROGENICS Advanced Hydrogen Solutions
4 DTU Technical University of Denmark

supported by: New Energy World JU fuel cells & hydrogen for sustainability

Overview presentation

- Project Overview
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- Motivation
- Problem to be solved: gas purity
- Project Approach: „E-by-pass separator“
- Problem to be solved: electrode efficiency and stability
- Project Approach: VPS Raney Nickel coating
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- Electrolyer System and BOP
- Summary

Project Overview

- “Hydrogen from RES: pressurised alkaline electrolyser with high efficiency and wide operating range”
- Duration Nov. 2011 – Oct. 2014
- Total budget: 2.89 Mio. €, FCH-JU contribution: 1.48 Mio. €; Regional support: 594,000 DKK from ForskEl program of Energinet.dk
- Consortium:

  DLR Dt. Zentrum f. Luft- und Raumfahrt - Germany (coordinator)

  VITO Vlaamse Instelling voor Technilogisch Onderzoek N.V. - Belgium

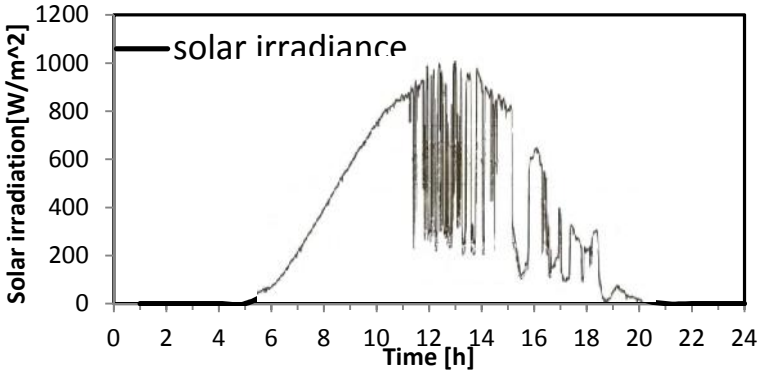
  Hydrogenics Europe NV – Belgium

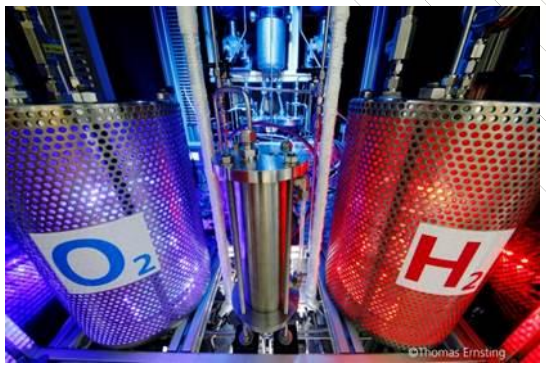
  DTU Danmark Techniske Universitet, Risoe Lab - Denmark

Project Overview

The project develops **high pressure**, **low cost** alkaline water electrolysers that can be integrated with **renewable power sources** using

- an advanced membrane concept,
- highly efficient electrodes
- and a new cell concept





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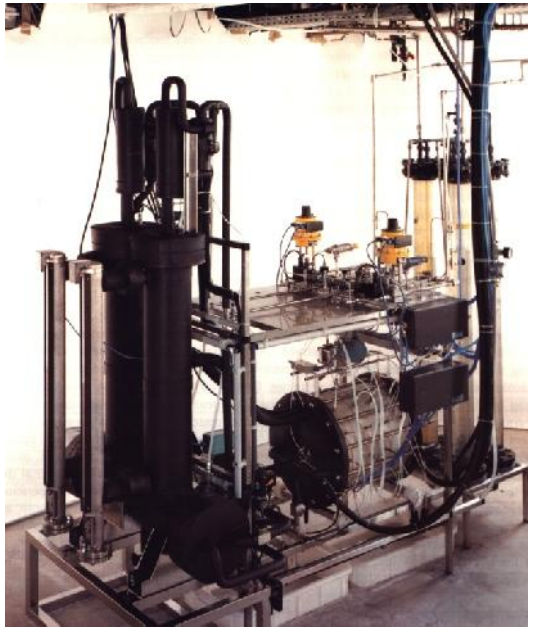
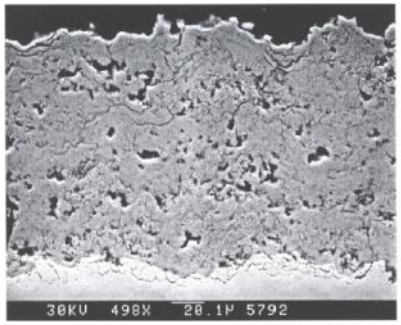
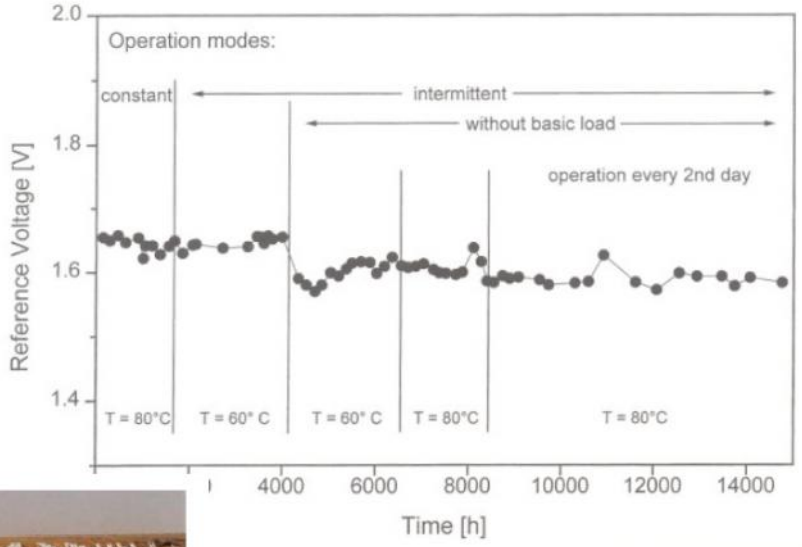
Project partners: DLR

DLR has a long background of alkaline electrolysis research from electrodes to systems.

HYSOLAR project 1985-1997







350 kW solar hydrogen production demontration plant

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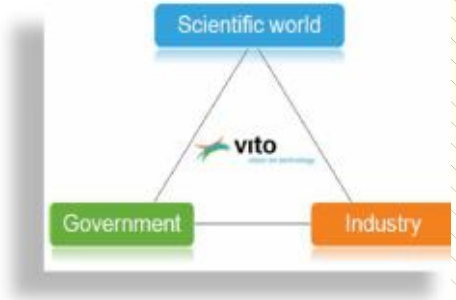
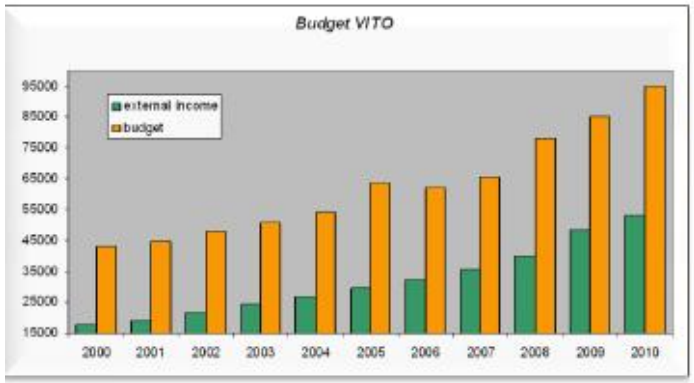
Project partners: DLR

DLR coordinates or participates in several PEM-Electrolysis projects in Germany

Study Over-view	**Plan-DelyKaD** (BMWE) 14 months Investigation of cost effective electrolysis systems with hydrogen storage in salt caverns	KBB, ludwig bölkow systemtechnik, DLR TT-STB, Fraunhofer ISE
Experimental and scientific-technical modelling	**LastElSys** (BMUB) 3 years Improvement of efficiency and durability in intermittent operation	HYDROGENICS
	WESpe (BMWE) 3.5 years Modelling and experimental validation of electrolysis systems	b-tu, DBI GUT, Deutsche Umwelthilfe, Fraunhofer ISE, DLR TT-STB
	KompElSys (BMVI) 3 years Development of cost-effective components for PEM-electrolysis	e·on, SolviCore, Fraunhofer ISE, HYDROGENICS
	Talstraße (LMU BW) 3 years System integration study PEM electrolysis at fuelling stations	HYDROGENICS, EnBW

Project partners: VITO





Facts & Figures

- Founded in 1991
- Autonomous public research company
- Bridge between academia – government and industry
- 5-year framework contract
- Nearly 600 people, 10 nationalities
- Yearly budget of 70 MEUR

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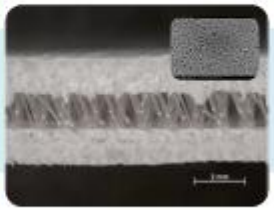
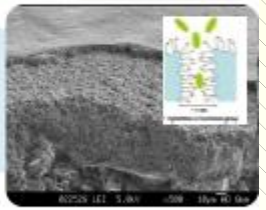
Project partners: VITO

Membrane/module development

- Casting and spinning of polymeric membranes
- Functionalisation of ceramic NF
- New module concepts
- **Separators and electrodes**





Membrane application testing/development

- MF, UF, NF, RO, PV, ED, MBR
- Solvent resistant NF
- Membrane distillation

Extraction

- Supercritical technology
- Biomass downstream processing
- Detection and isolation of high value compounds

Project partners: Hydrogenics

- Provider of clean solutions based on hydrogen
- 120 employees
- Listed on NASDAQ (HYGS) and TSX (HYG)
- Sales offices, R&D & Production facilites:
  - Canada (HQ): Fuel Cells
  - Belgium: Water Electrolyzers & Systems Integration
  - Germany: Fuel Cell Systems
  - Sales & Service offices: China, India, Russia
- + 1,700 products deployed worldwide since 1948

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Project partners: Hydrogenics

Lines of business:

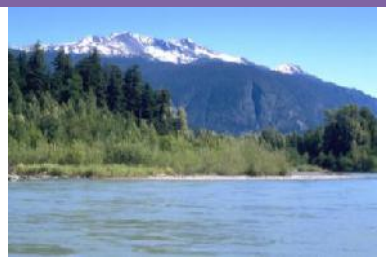
Onsite Generation
Water Electrolyzers

Industrial hydrogen | Hydrogen fueling

Power Systems
Power Modules

Backup power | Mobility power

Energy Storage



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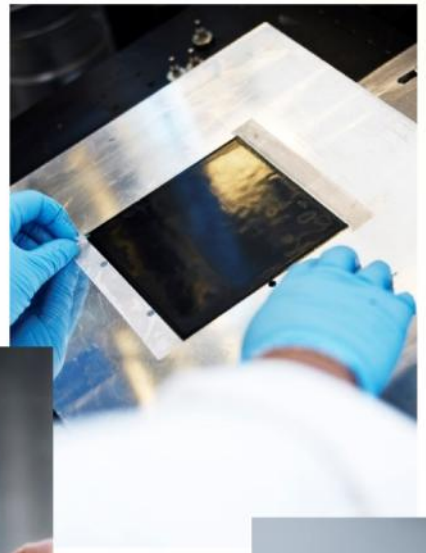
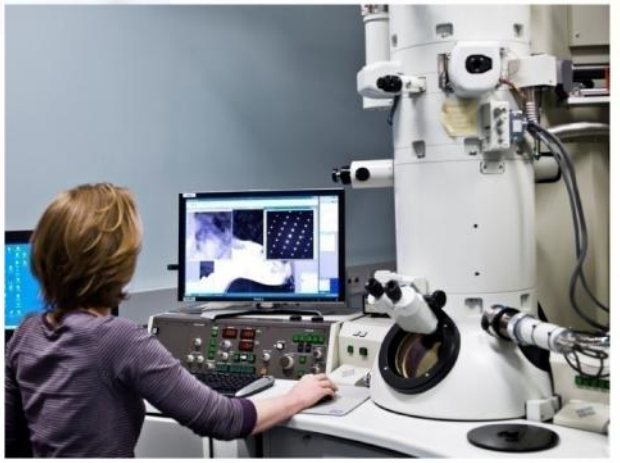
Project partners: DTU

- DTU Risoe now „DTU Energy conversion“

Research and Competences:

– Ceramic processes
– Scale-up
– Materials development
– Characterization
– Advanced test
– Modelling
– Technology transfer

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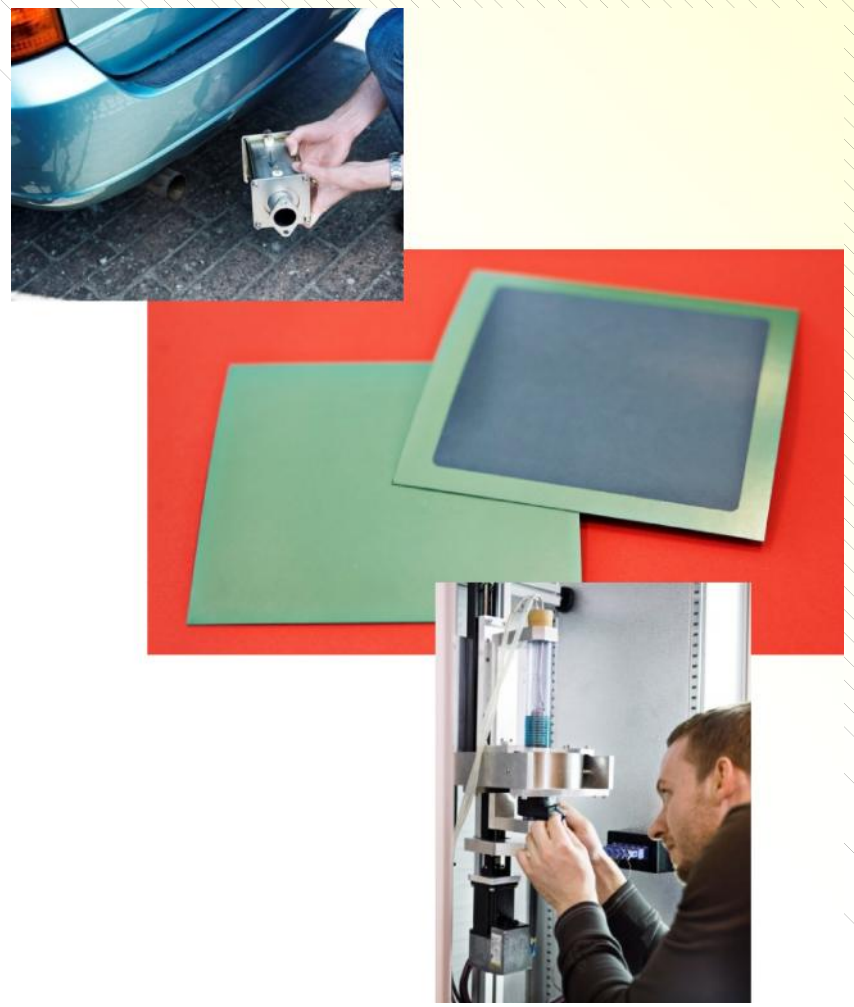
Project partners: DTU

- Fuel cells (SOFC)
- Electrolysis (SOEC and AEC)
- Magnetic refrigeration
- Membranes for oxygen or hydrogen separation
- Electrochemical flue gas purification
- Thermoelectrics
- Batteries
- Test and approval centre:

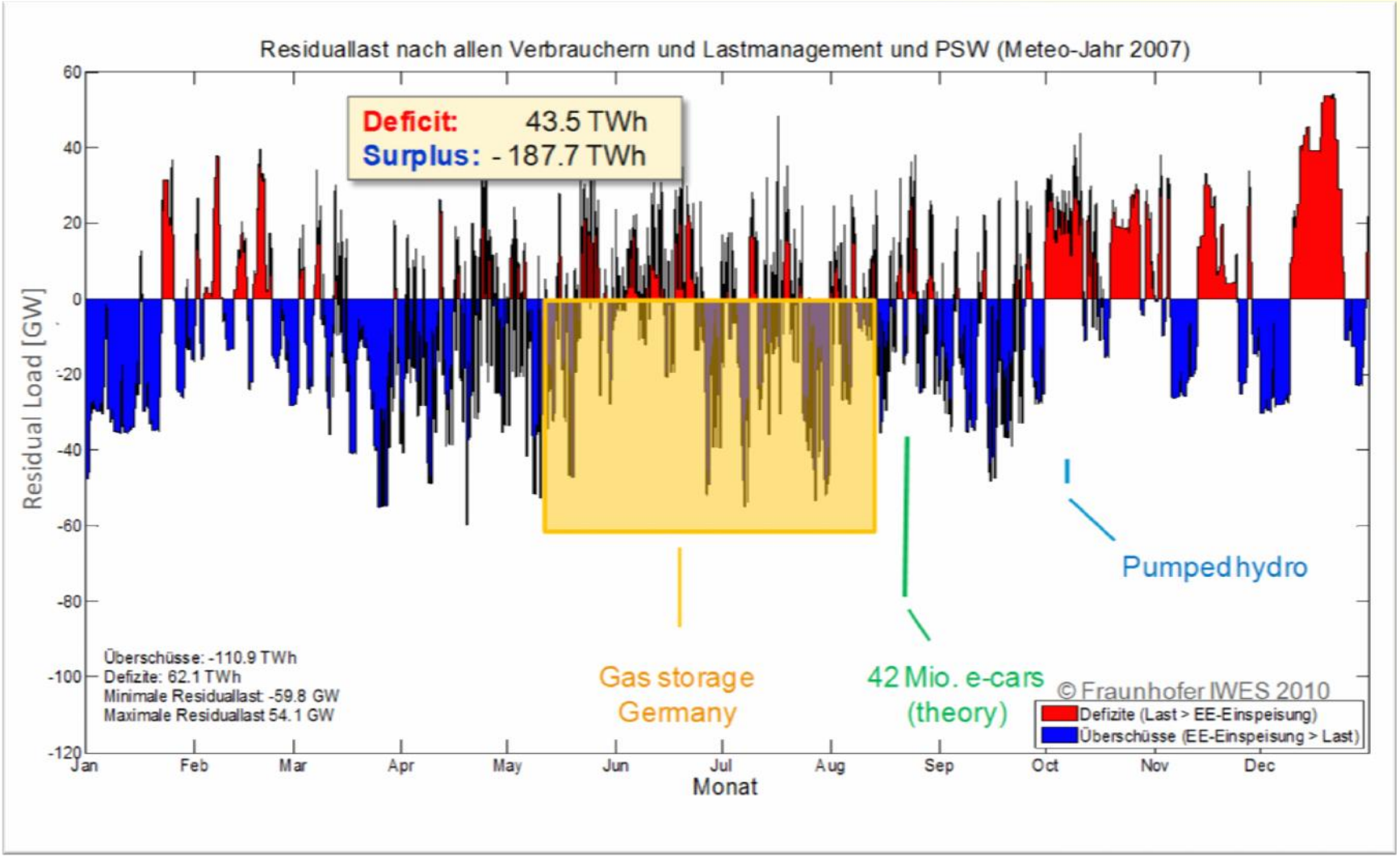
  Fuel cells and hydrogen technologies



Technical University of Denmark

Motivation

- Unique feature of storing energy as a chemical

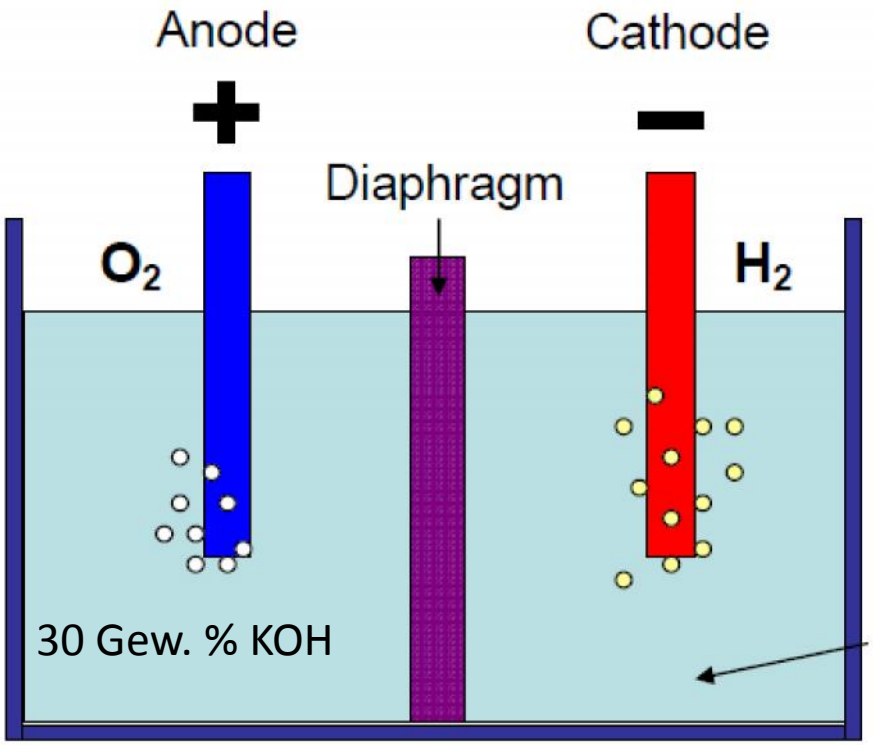


Motivation

- Intermittent Renewable Sources wind and solar - preferred route for future european energy mix
- Intermittent production needs storage technologies
- Grid stabilization – Renewable integration
- Building blocks for MW alkaline electrolysis
- Dynamic operation – rapid response
- Idle – production – power based steering
- Extending range of operation 10%-100% -> 1%-120%
- Higher pressure
  - Skip compression stages for H_2 fueling
- Higher efficiency without lowering output
  - Coatings
  - Cost/performance – business modelling

Motivation

Alkaline water electrolysis



$$H_2O \Rightarrow H_2 + \tfrac{1}{2} O_2$$

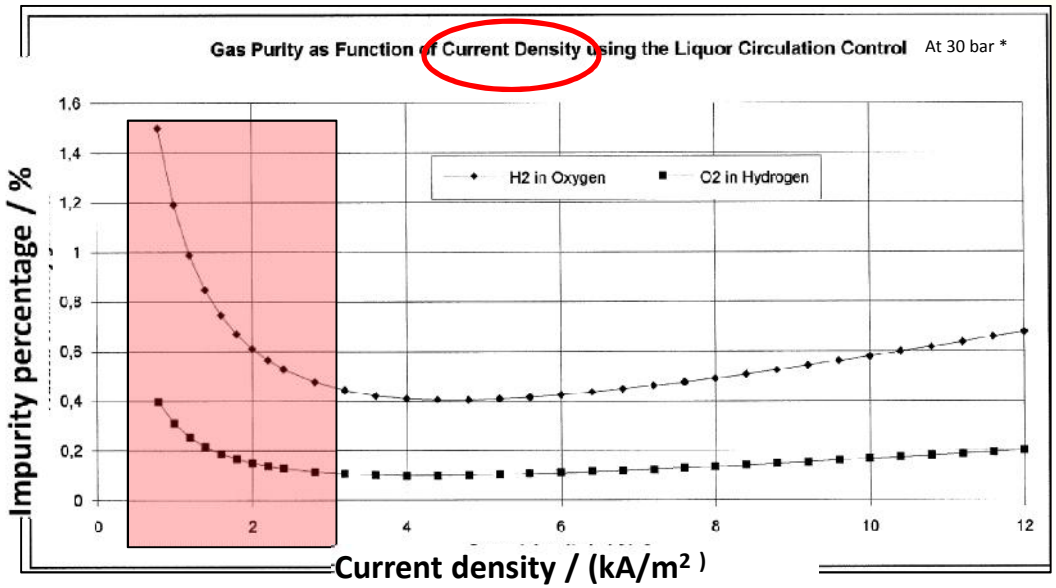
Cathode: $2H_2O + 2e^- \Rightarrow H_2 + 2HO^-$

Anode: $2HO^- \Rightarrow \tfrac{1}{2} O_2 + H_2O + 2e^-$

- Well established technique up to large scale systems
- Cheap materials
- Gas purity problems at low load and high pressure
- Electrode stability when electrolyser off
- System adaptation to use with RES

Problem to be solved: Gas purity

High H_2 impurity in oxygen at low power and high pressure → safety problem anode gas



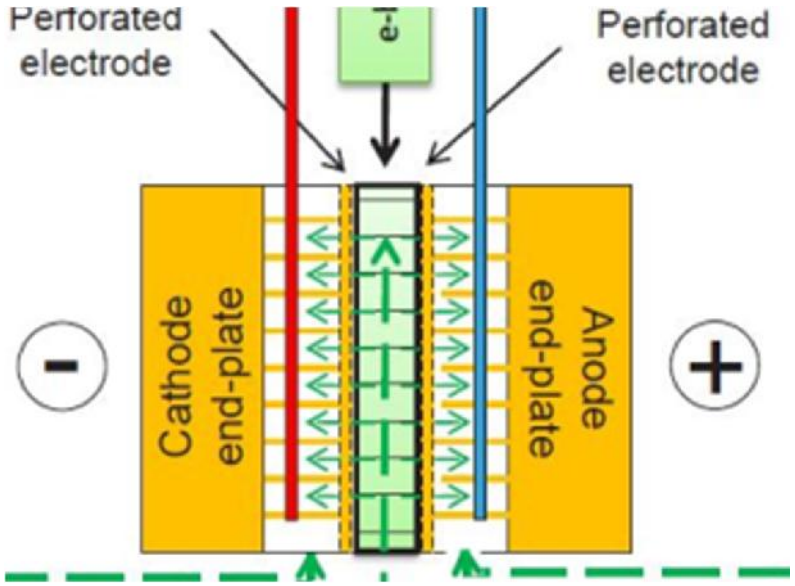
* C.A. Schug, Int J. Hydrogen Energy 23 (12) (1998) 1113

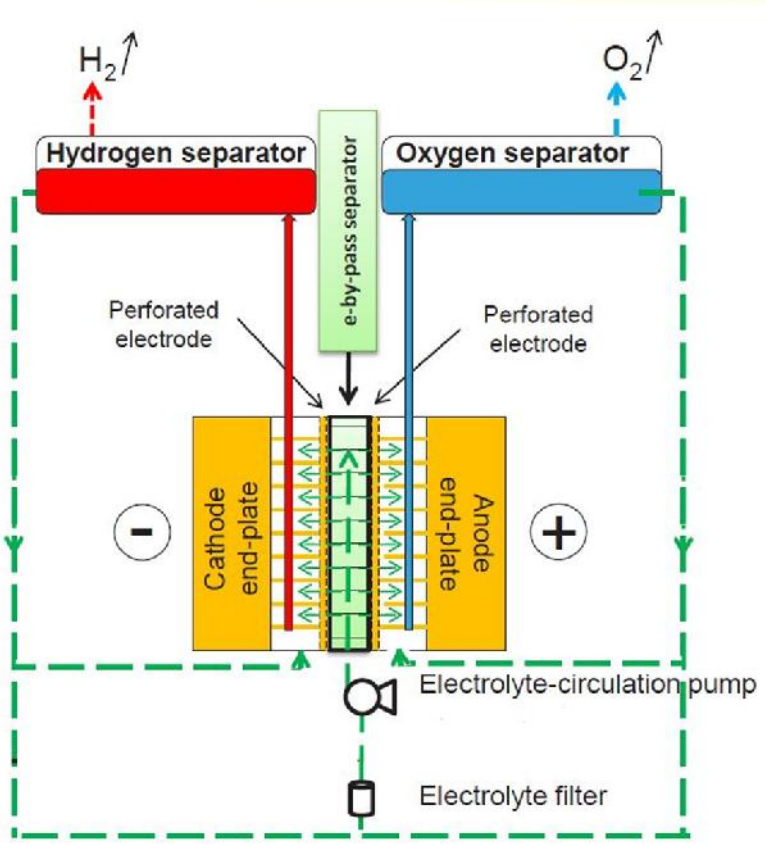
Reason for the problem:

- Diffusion of H_2 in O_2 und O_2 in H_2 dissolved in electrolyte depending on T, p
- At low current density and at high pressure H_2 to O_2 ratio becomes too high

Project approach: „E-by-pass separator“

- double layer diaphragm with internal KOH supply (“E-by-pass separator”) and adapted cell concept (3 compartment electrolyser)





Project approach: „E-by-pass separator“

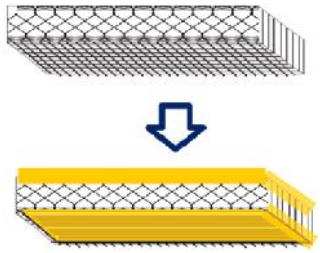
Goals: develop the “E-by-pass separator” diaphragm with internal electrolyte bypass

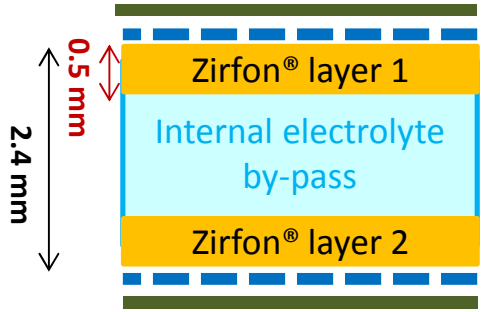
and properties for maximum benefit of the cell

develop technical scale fabrication methods

Progress achieved: double side coated PPS spacer-fabric

- Various thicknesses realised: total thickness approx. 2.4mm to 2.9mm
- Zirfon®(ZrO_2/polymer composite) dual layer, each layer ca. 0.5 mm.
- interposed free electrolyte channel ca. 1.5 mm
- Variation of permeability: from 120 l/(h m^2 bar) to 900 l/(h m^2 bar)





Project approach: „E-by-pass separator“

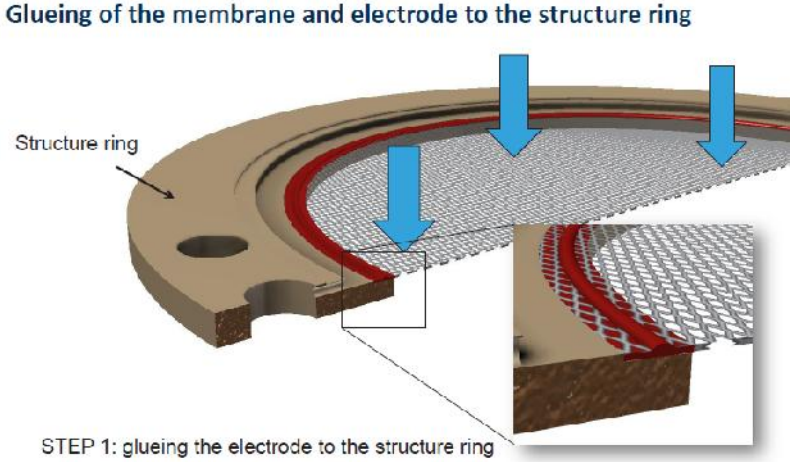
Progress achieved:

- Separator of 300 cm^2 delivered for cell and stack integration
- Technical scale (2500 cm^2) producibility demonstrated; relevant physico-chemical properties (R, Lp, BP) maintained upon upscaling

Project approach: „E-by-pass separator“

Cell construction integrating the e-by-pass separator –

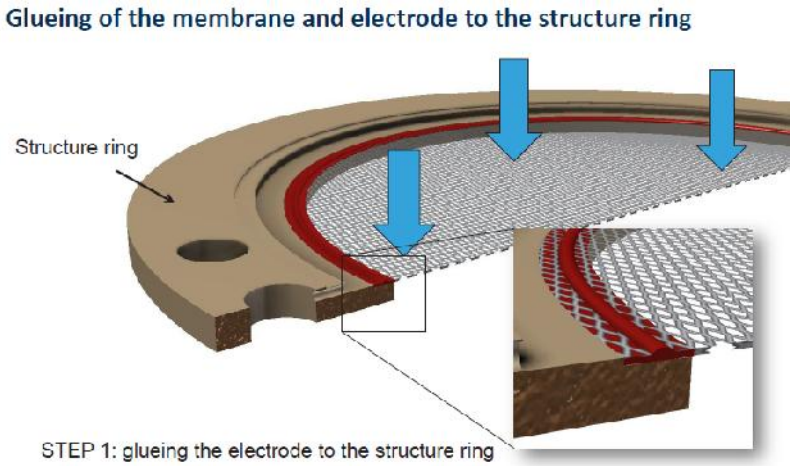
Concept 1 Glue concept

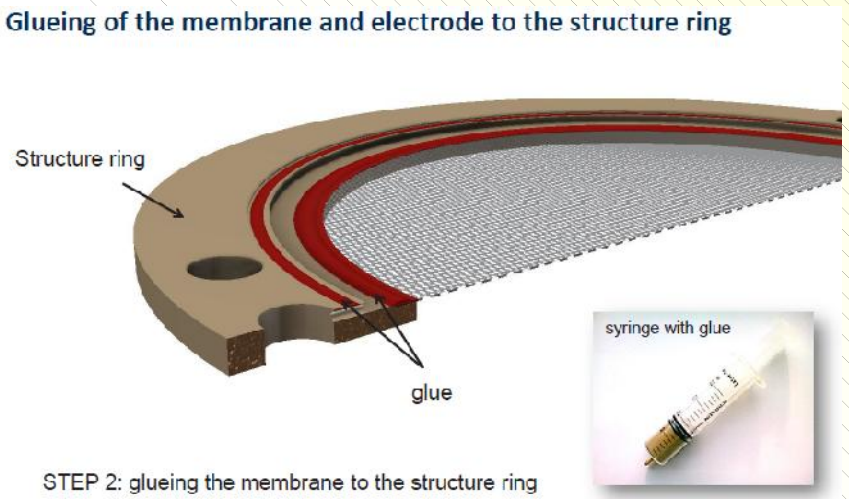


Project approach: „E-by-pass separator“

Cell construction integrating the e-by-pass separator –

Concept 1 Glue concept

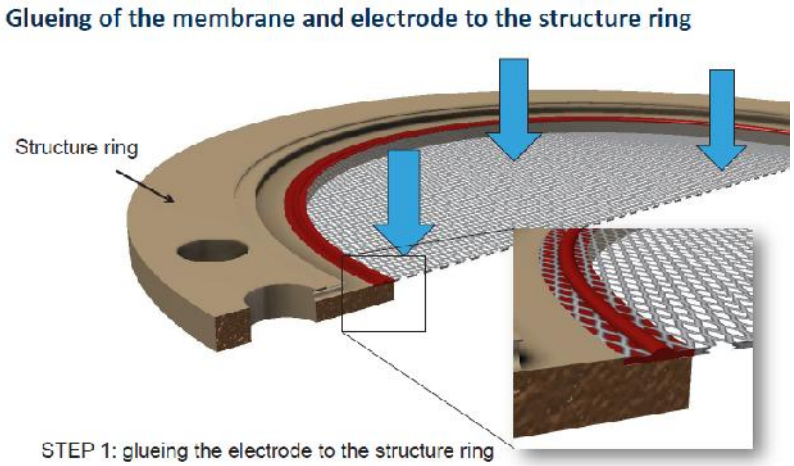


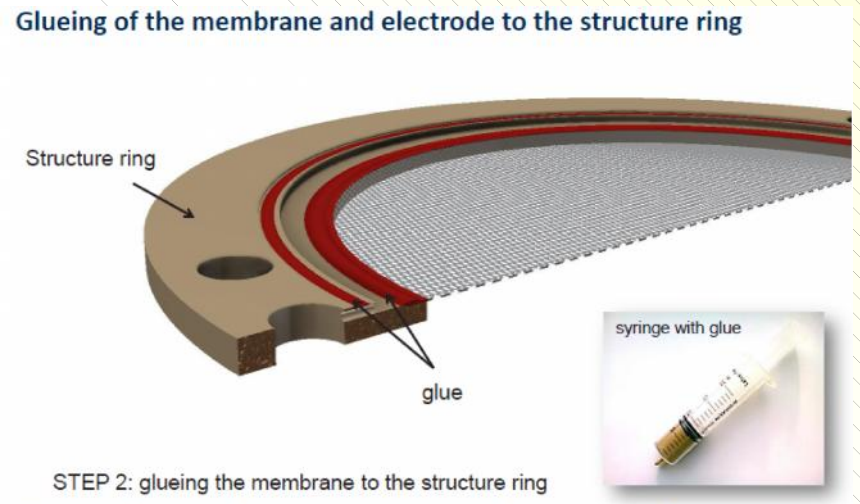


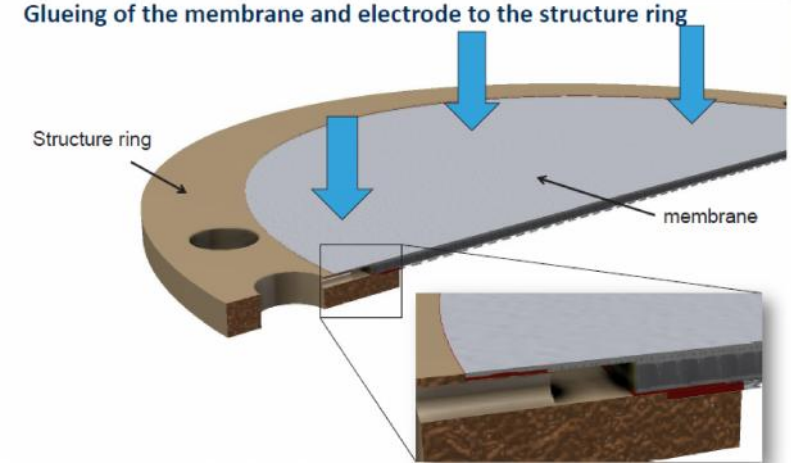
Project approach: „E-by-pass separator“

Cell construction integrating the e-by-pass separator –

Concept 1 Glue concept



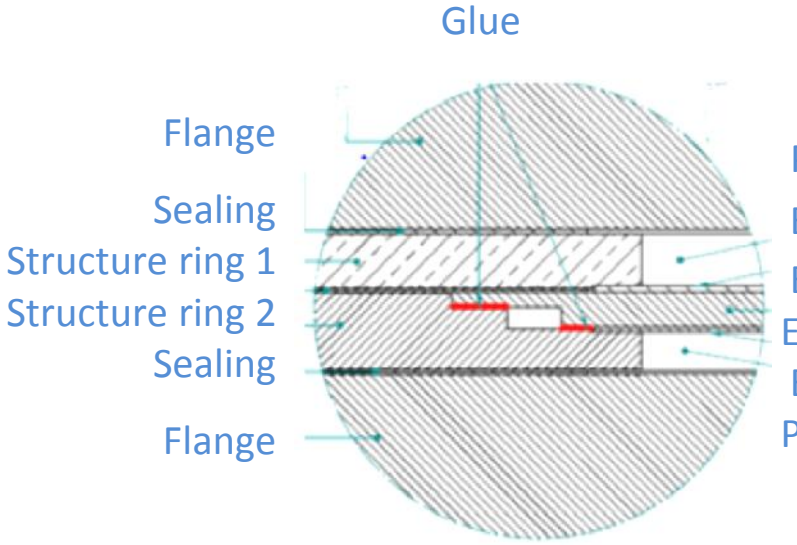


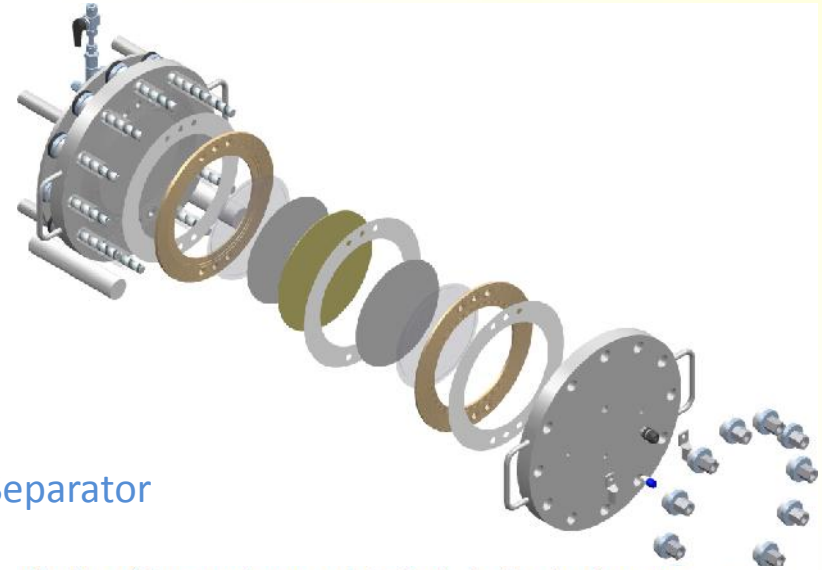


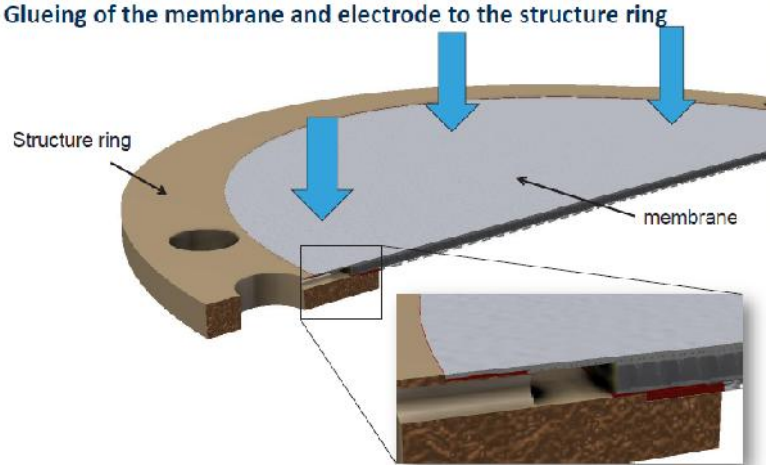
Project approach: „E-by-pass separator“

Cell construction integrating the e-by-pass separator –

Concept 1 Glue concept

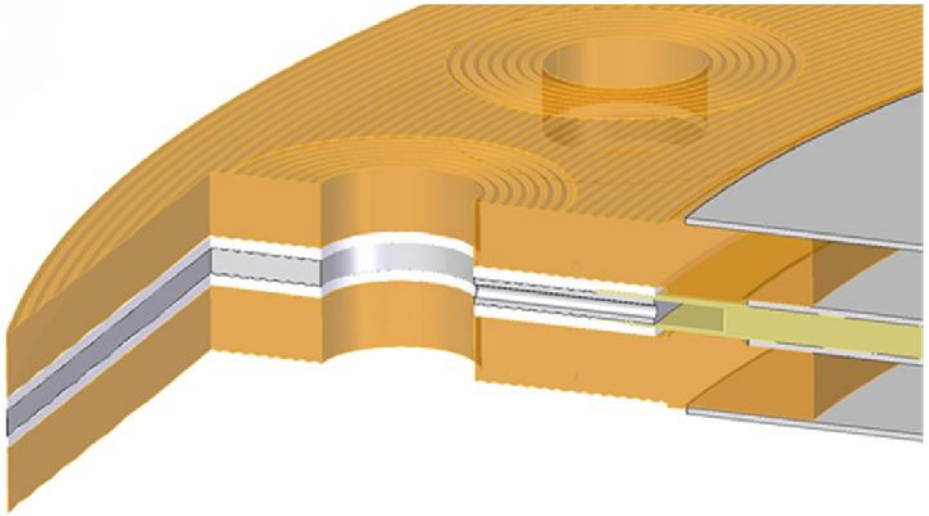


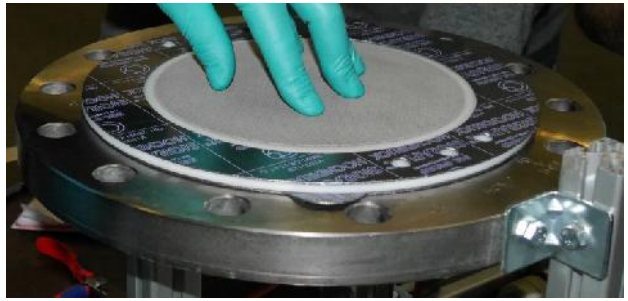


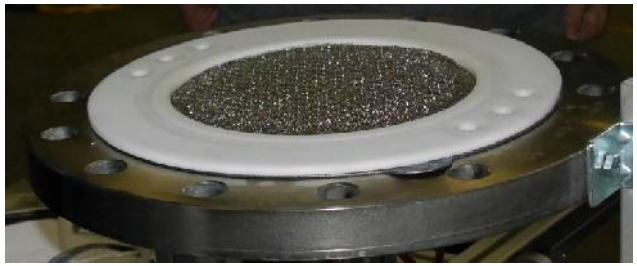


Project approach: „E-by-pass separator“

Cell construction integrating the e-by-pass separator – Concept using graphite seals







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Problem to be solved: electrode efficiency and stability

State of art low cost electrodes: Nickel or Ni coated Fe

Deactivation by:

- Nickel-corrosion
- Absorption of hydrogen with formation of hydride
- Adsorption of organic impurites (mostly from lye or separator)
- Deposition of metals (e.g. Fe),

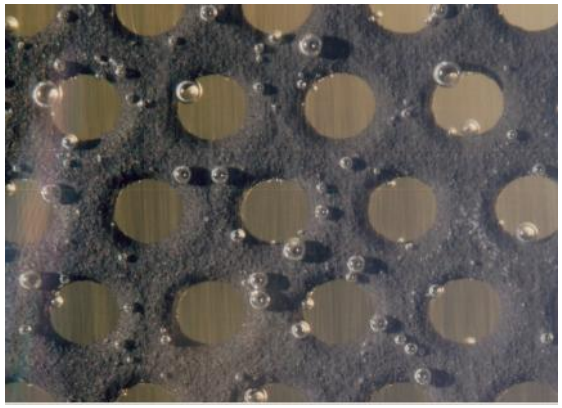
Better results using:

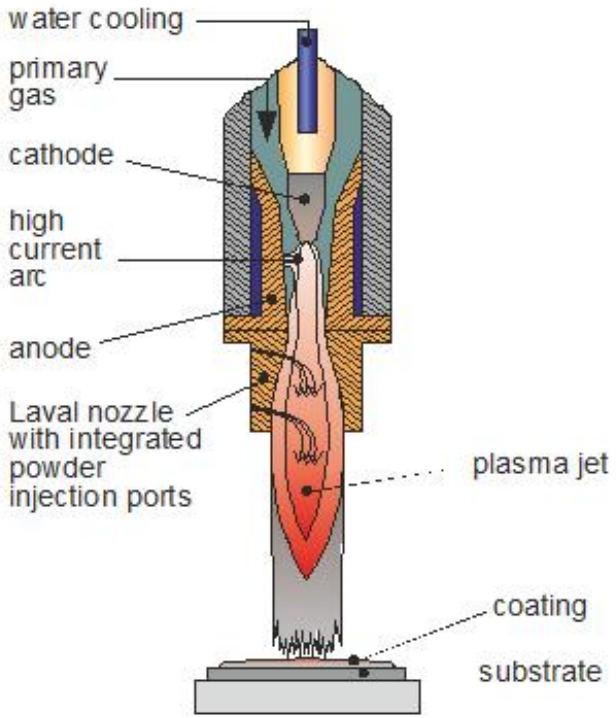
- Noble metal catalysts like Pt with high surface
- Ruthenium oxide (RuO_2)
- Raney-Ni und Ni-alloys, especially NiMo

Project approach: VPS Raney Ni coating

Electrode development for low overpotential, long life-time and low costs

Goal: Using the VPS coating, electrodes are developed with low-cost materials that have a high efficiency/low overpotential and little degradation in intermittent operation





Project approach: VPS Raney Ni coating

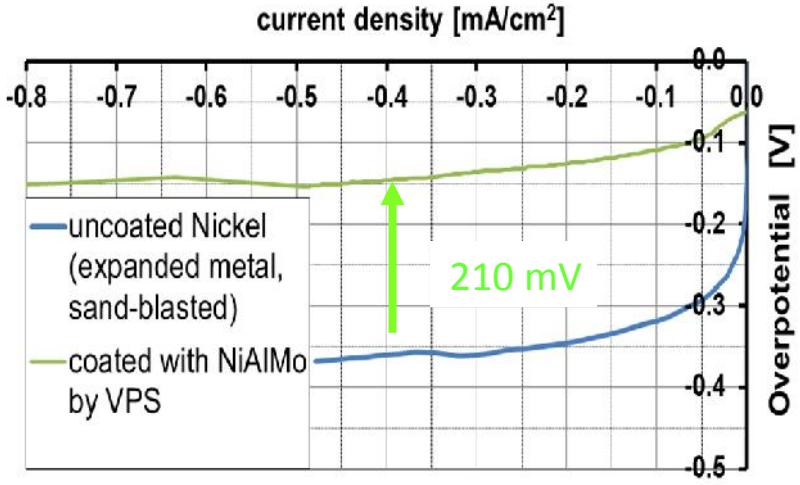
Electrode development for low overpotential, long life-time and low costs

Progress achieved:

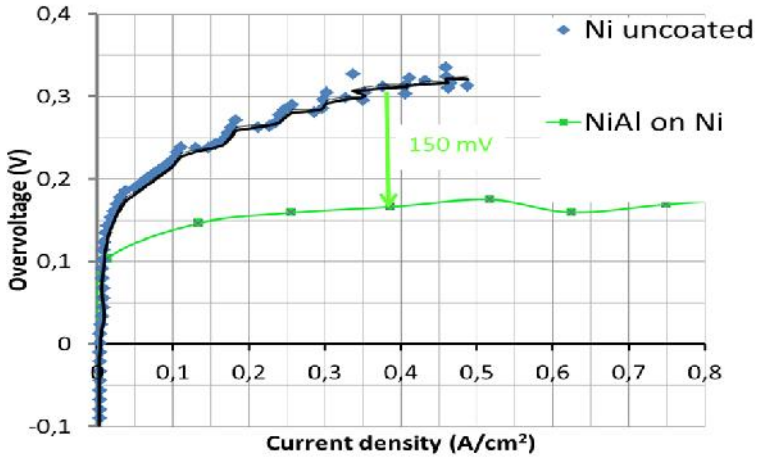
Overpotential reduction to uncoated Ni electrode:

Cathode 210 mV using NiAlMo coating

Anode 150 mV for NiAl



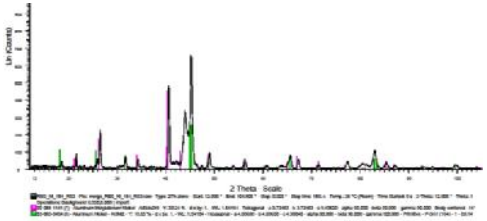
Half cell measurement 70°C in 35 % KOH, potentials IR-corrected



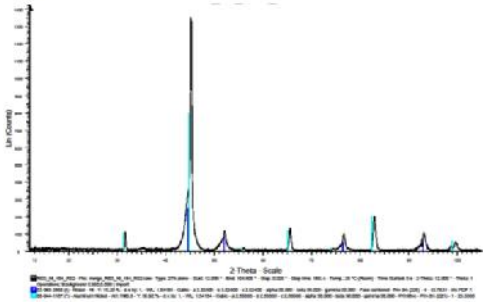
Project approach: VPS Raney Ni coating

Al is removed by leaching, high Ni surfaces are opened

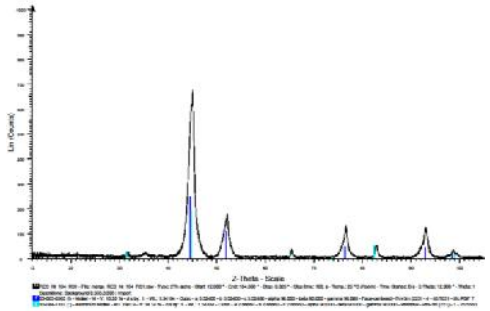
XRD metal phase composition:



NiAlMo-coated electrode after coating: many different phases $Ni_xAl_yMo_z$

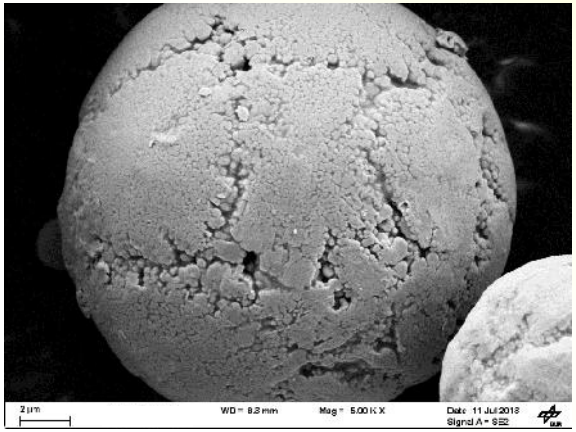


Leached at 80°C: still clear NiAl signal

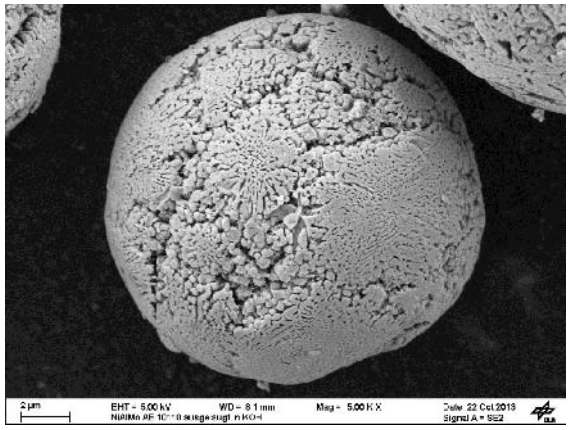


Leached at 90°C: mostly Ni

SEM image original powder



SEM image leached, activated powder:



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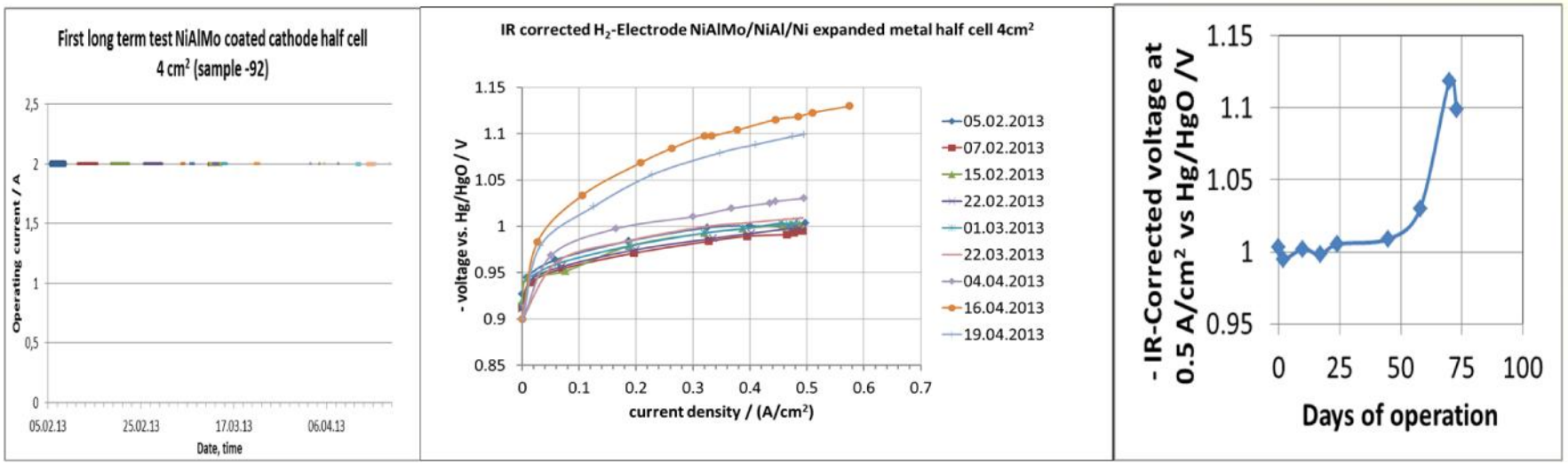
Project approach: VPS Raney Ni coating

Long term test of first generation of NiAlMo coated cathodes:

Serious degradation and layer delamination after 10 days period at OCV (half cell test)

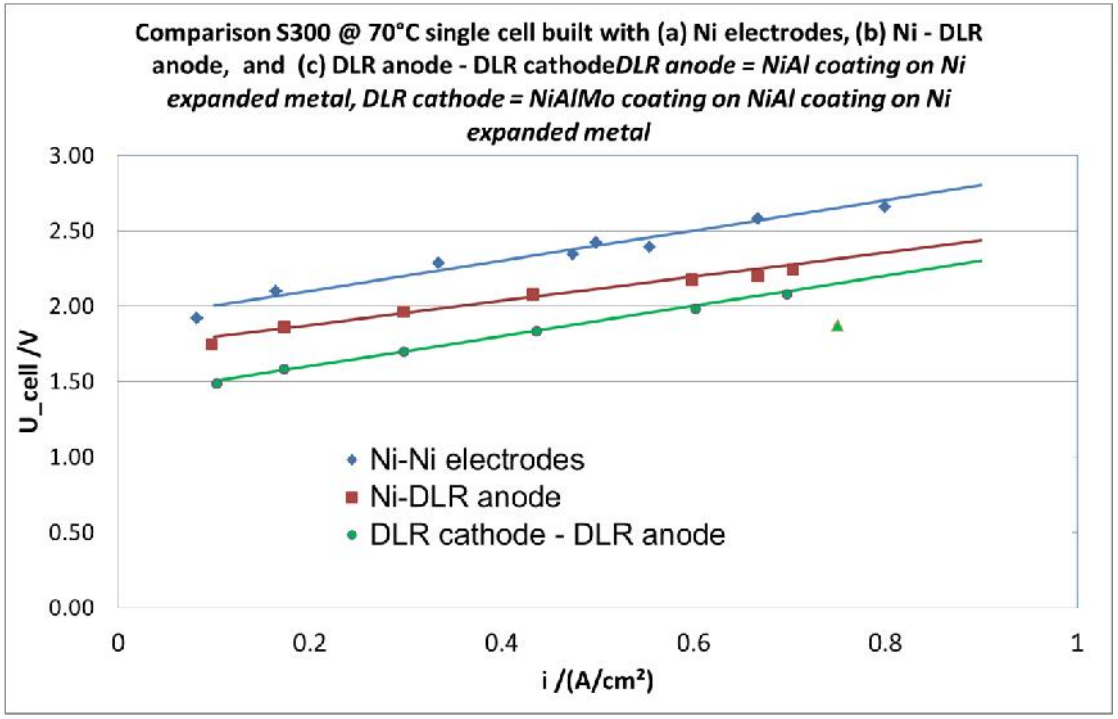


Improved by changing plasma spray parameters

Project approach: VPS Raney Ni coating

Full cell test 300 cm²:

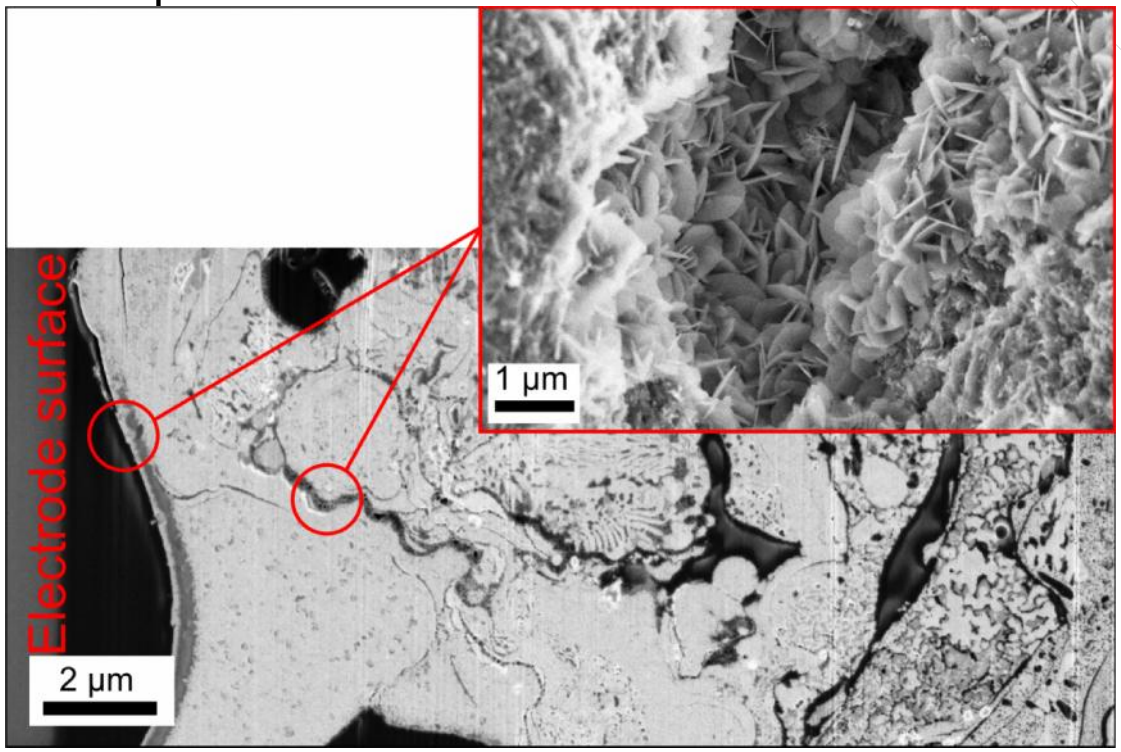
serious efficiency improvement when going from uncoated to coated electrodes.



Project approach: VPS Raney Ni coating

Characterisation of porosity of unused and used electrodes by 3D SEM reconstruction

Goal: understanding the mechanisms in electrode degradation due to evolution of the pore size distribution



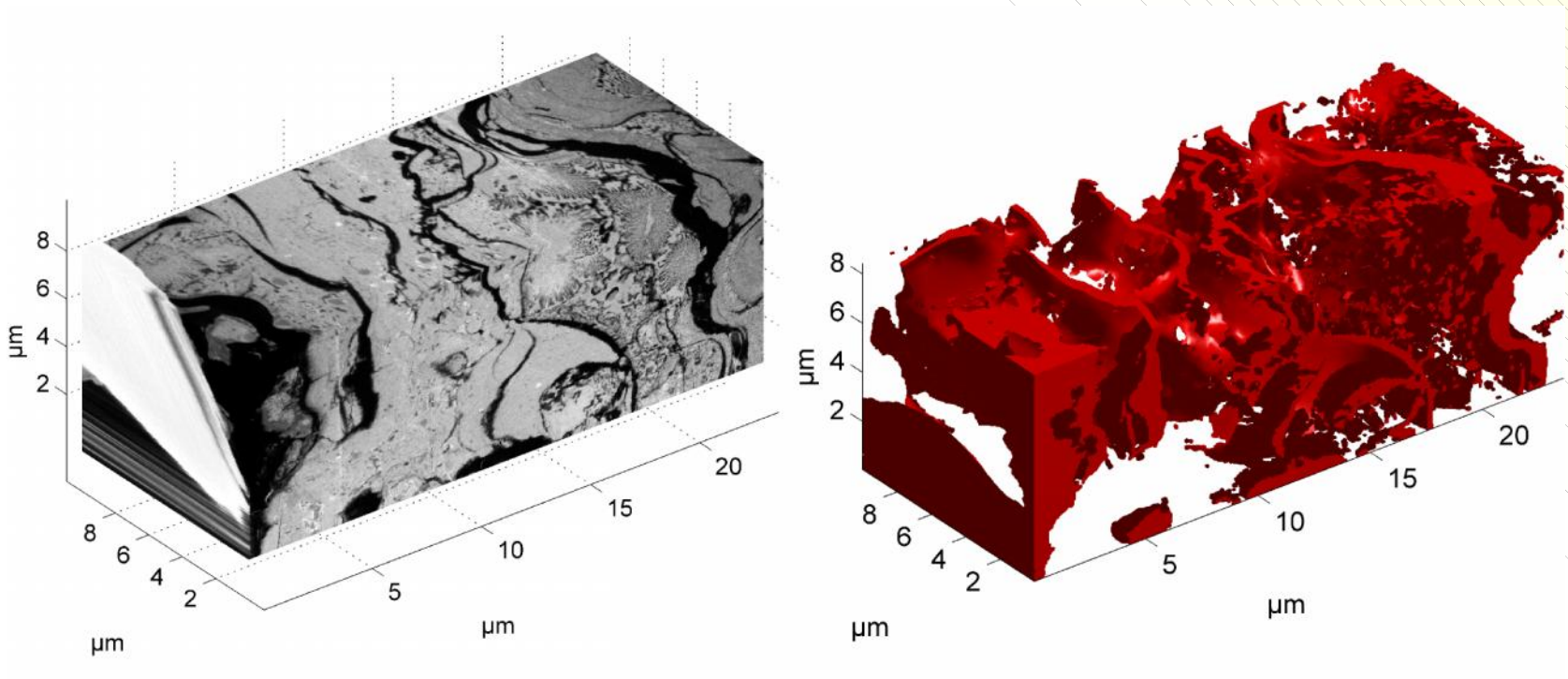
Electrode microstructure

- Highly heterogeneous microstructure with many subdomains.
- Dendritic structures stemming from the dissolution of Al from the Raney type NiAl alloy particles.
- Desert rose like nano flake structures (NiO and Al_2NiO_4 like phases) observed in the pores of several samples.
- Implications and causes still being investigated.

Project approach: VPS Raney Ni coating

3D reconstruction of the electrode pores

- Coarse scale planar like pores parallel to the electrode surface.
- Significant pore volume fraction of sub 100 nm wide pores in the dendritic structure.



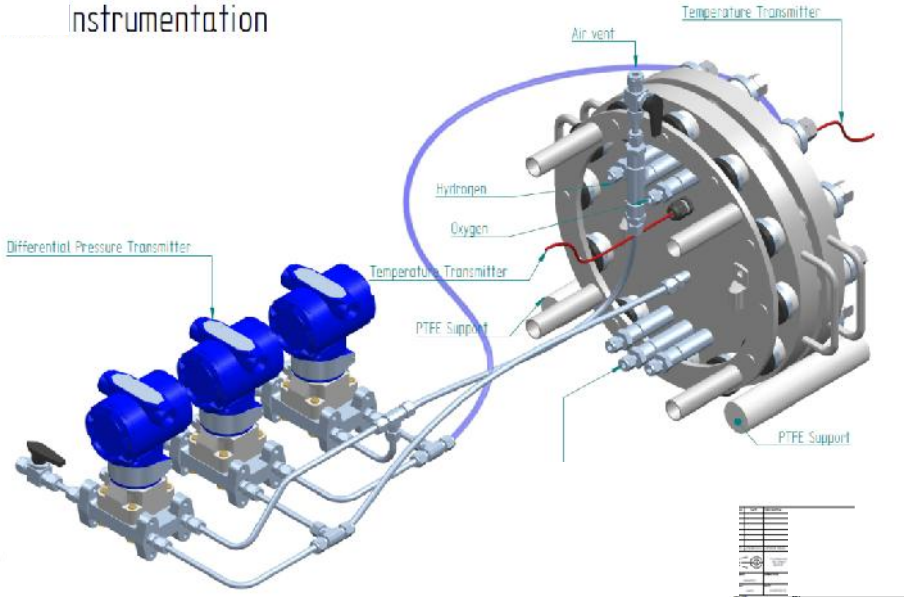
Technical University of Denmark

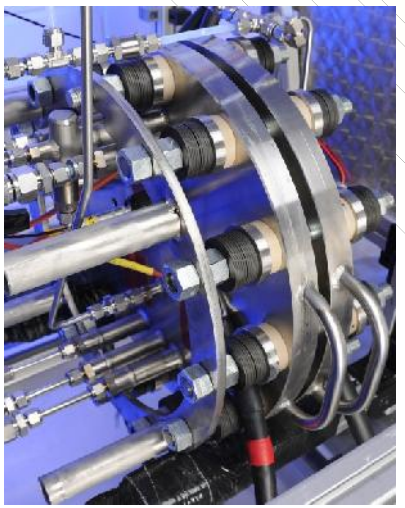
Cell and Stack Construction

Single cell, 10 kW and 30 kW stack development, construction and test

Goal: realisation of electrolysers with the new concept up to technical size, up to 25 bar, concept development for 150 bar

Progress achieved: Cell concept developed and construction ready for single cell with double layer membrane





HYDROGENICS
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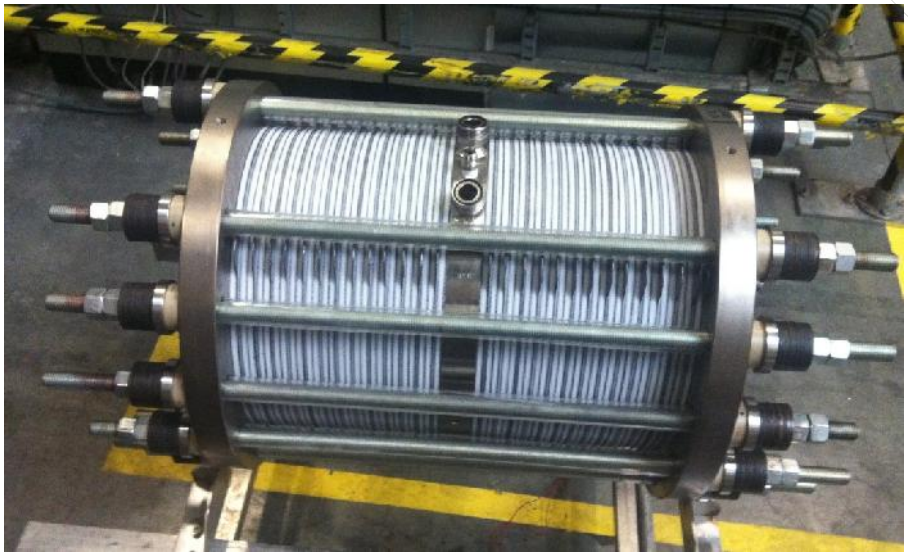
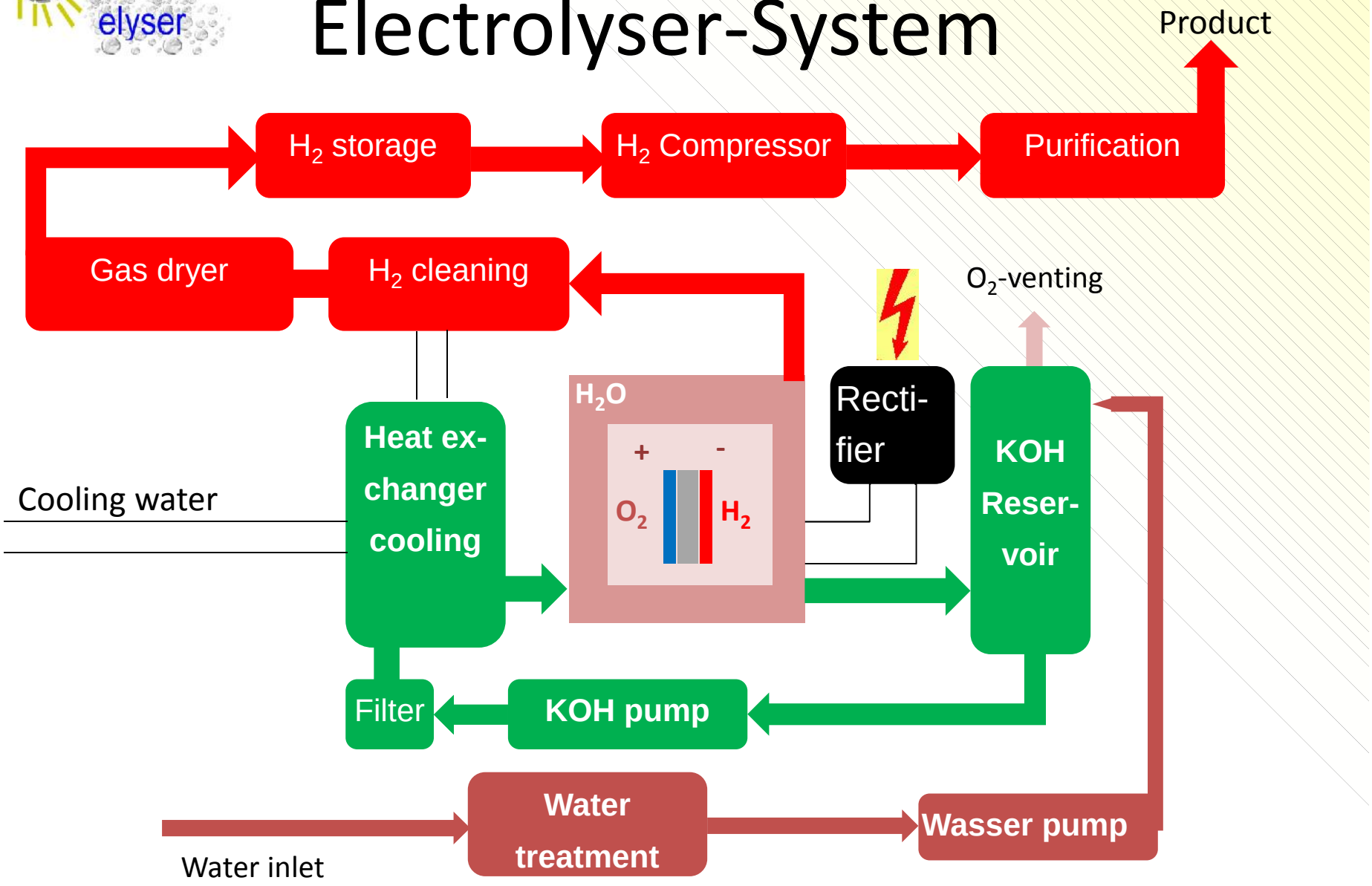
Cell and Stack Construction

- 10 kW stack with e-by-pass membrane and Plasma-spray coated electrodes to be operated up to 10 bar
- Cell stack leakproof, values of permeability from ex-situ measurements in good agreement with those determined in-situ

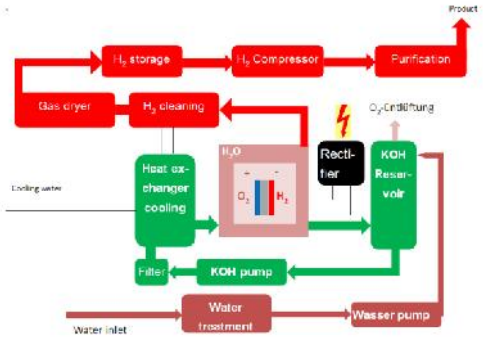


HYDROGENICS
Advanced Hydrogen Solutions

Electrolyser-System



Electrolyser-System



Improvements suggested to adapt to fluctuating power and reduce costs:

- Modular electrolyser (modules off or close to nominal power)
- High pressure -> no compressor
- Adapt IV-characteristics to IV-characteristics of renewable power supply (solar field..)
- Reduce number of components by higher system component integration
- Power changes induce internal pressure changes -> reduce by control
- Reduce power consumption of BOP components e.g. cooling
- Power control strategy of BOP componts in fluctuating operation

BOP and System

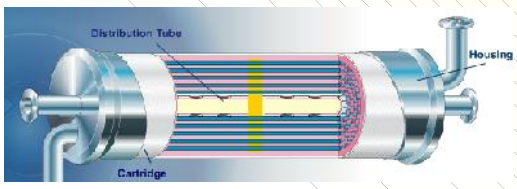
E-by-pass concept

needs additional electrolyte pump and electrolyte degassing

but no more H_2 compressor

Possible concepts for electrolyte degassing:

- Pressure release over KOH in flow towards cell + gas separator, subsequent pressurisation with feed pump
- Liqui-Cel® Membrane Contactor
- Ultrasonic treatment in gas separator



- Membrane filter with only liquid permeability to avoid micro-gas bubbles to remain in the electrolyte supplied to the pump
- Temperature increase of KOH in flow towards cell + gas separator

Summary, outlook

The RESelyser project adresses some of the points to make alkaline electrolysers even more fit to be integrated with fluctuating renewable energy sources

- Cost reduction
- Suitable for fast power fluctuations
- Fast startup, no problems with shutdown
- Long lifetime
- High efficiency

There is much more potential for improvement of alkaline electrolysers than what can be worked out in one project

Thank you for your attention

www.reselyser.eu

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The end