



Hydrogen from Regenerative Energy Power Sources: pressurised alkaline electrolyser with high efficiency and wide operating range The Project „RESelyser“

R. Reissner¹, G. Schiller¹, E. Guelzow¹, Y. Alvarez Gallego², W. Doyen², A. Funke³, J. Vaes³, J.R. Bowen⁴ et al.

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Deutsches Zentrum
für Luft- und Raumfahrt e.V.
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Overview presentation

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- Project Approach: „E-by-pass separator“
- Problem to be solved: electrode efficiency and stability
- Project Approach: VPS Raney Nickel coating
- Cell and Stack Construction
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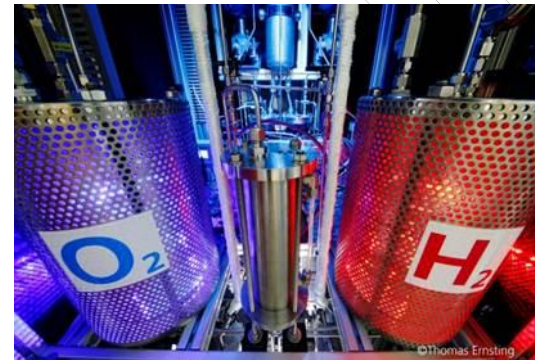
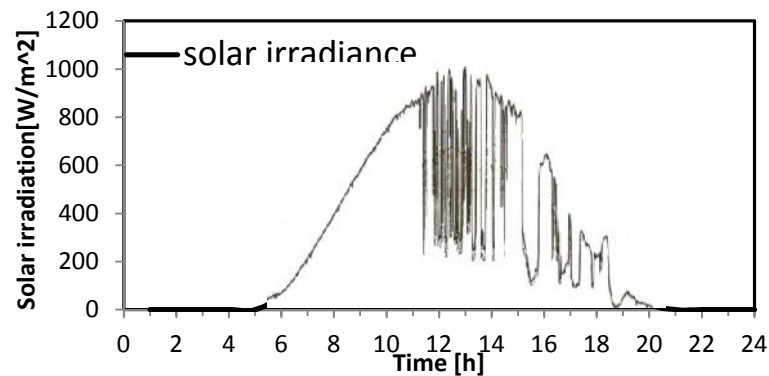
Project Overview

- “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 Technologisch Onderzoek N.V. - Belgium
 - Hydrogenics Europe NV – Belgium
 - DTU Danmark Technische Universitet, Risoe Lab - Denmark

Project Overview

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

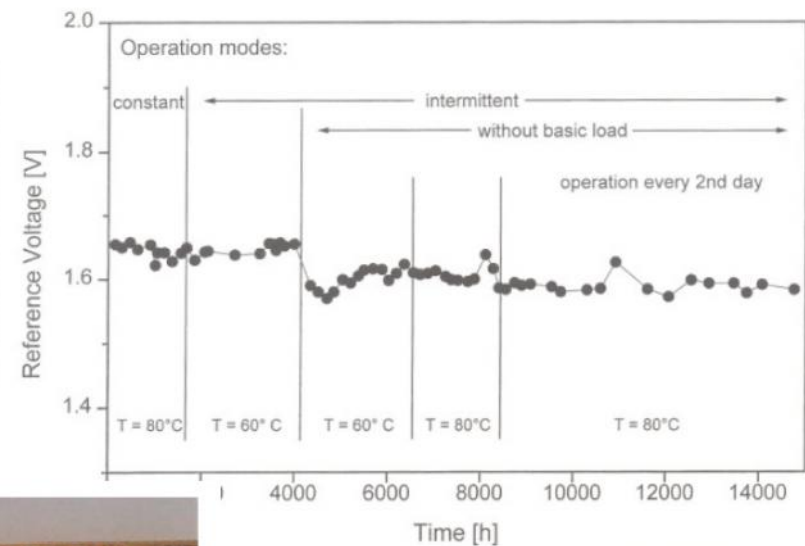
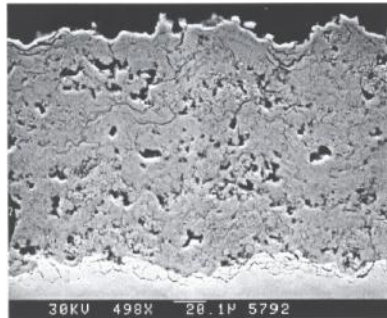
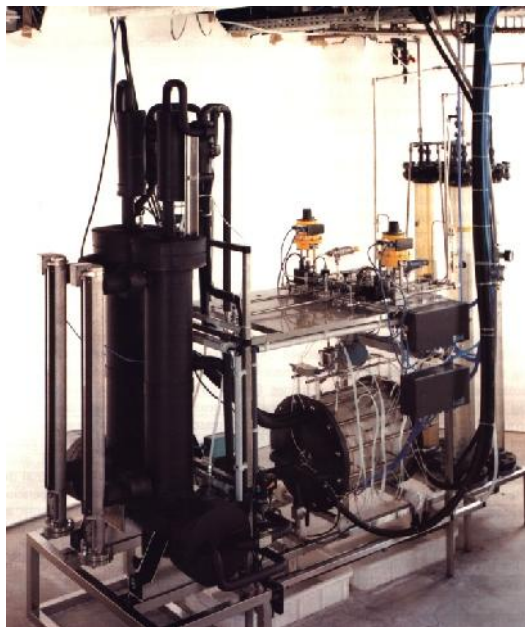
- an advanced membrane concept,
- highly efficient electrodes
- and a new cell concept



Project partners: DLR

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








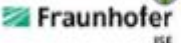








HYSOLAR project 1985-1997



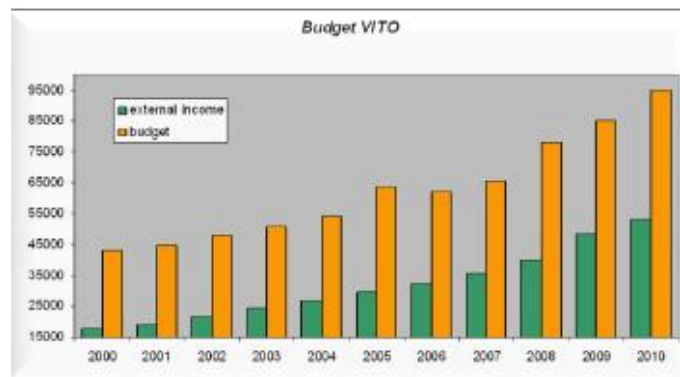
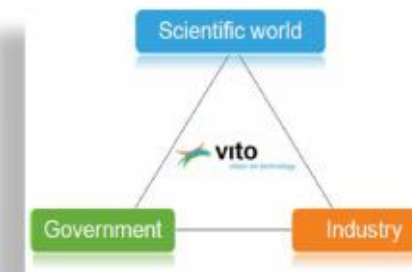
350 kW solar hydrogen
production demonstration plant

Project partners: DLR

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

Study Over-view	Plan-DelyKaD (BMW) 14 months Investigation of cost effective electrolysis systems with hydrogen storage in salt caverns	   
Experimental and scientific-technical modelling	LastElSys (BMUB) 3 years Improvement of efficiency and durability in intermittent operation	
	WESpe (BMW) 3.5 years Modelling and experimental validation of electrolysis systems	    
	KompElSys (BMVI) 3 years Development of cost-effective components for PEM-electrolysis	   
	Talstraße (LMU BW) 3 years System integration study PEM electrolysis at fuelling stations	 

Project partners: VITO



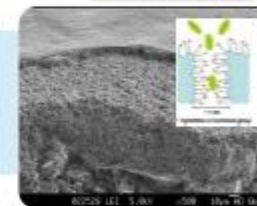
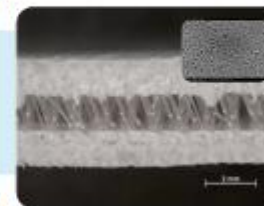
Facts & Figures

- 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

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



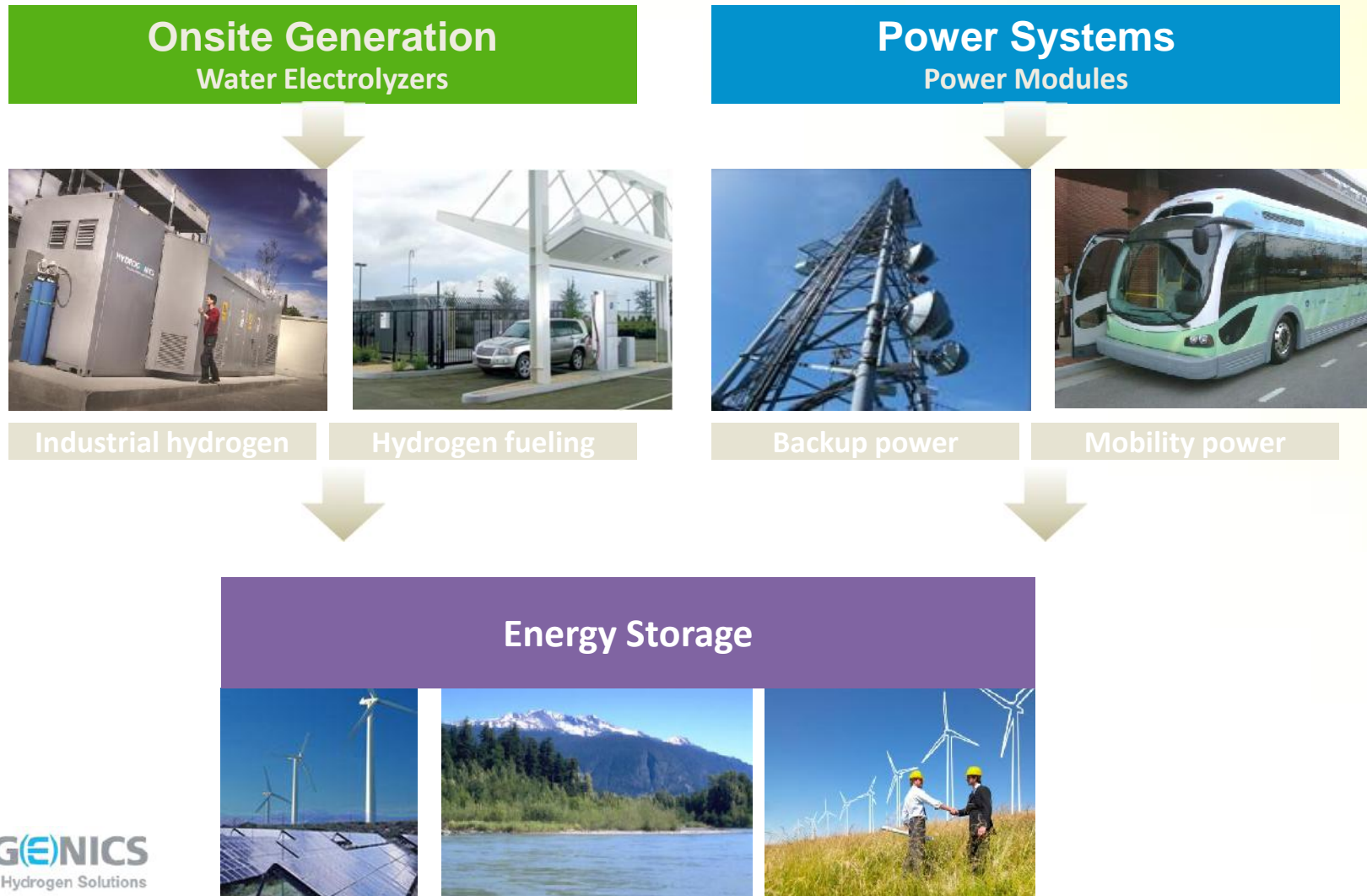
Project partners: Hydrogenics

- Provider of clean solutions based on hydrogen
- 120 employees
- Listed on NASDAQ (HYGS) and TSX (HYG)
- Sales offices, R&D & Production facilities:
 - 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



Project partners: Hydrogenics

Lines of business:

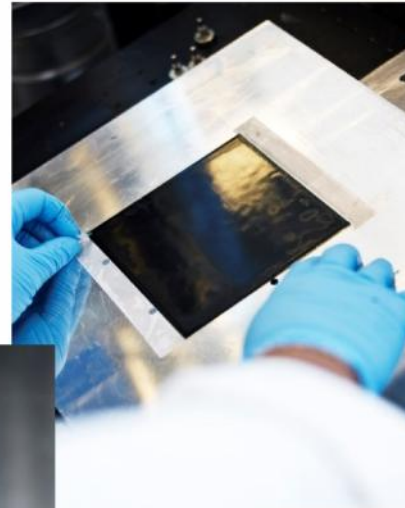


Project partners: DTU

- DTU Risoe now „DTU Energy conversion“

Research and Competences:

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



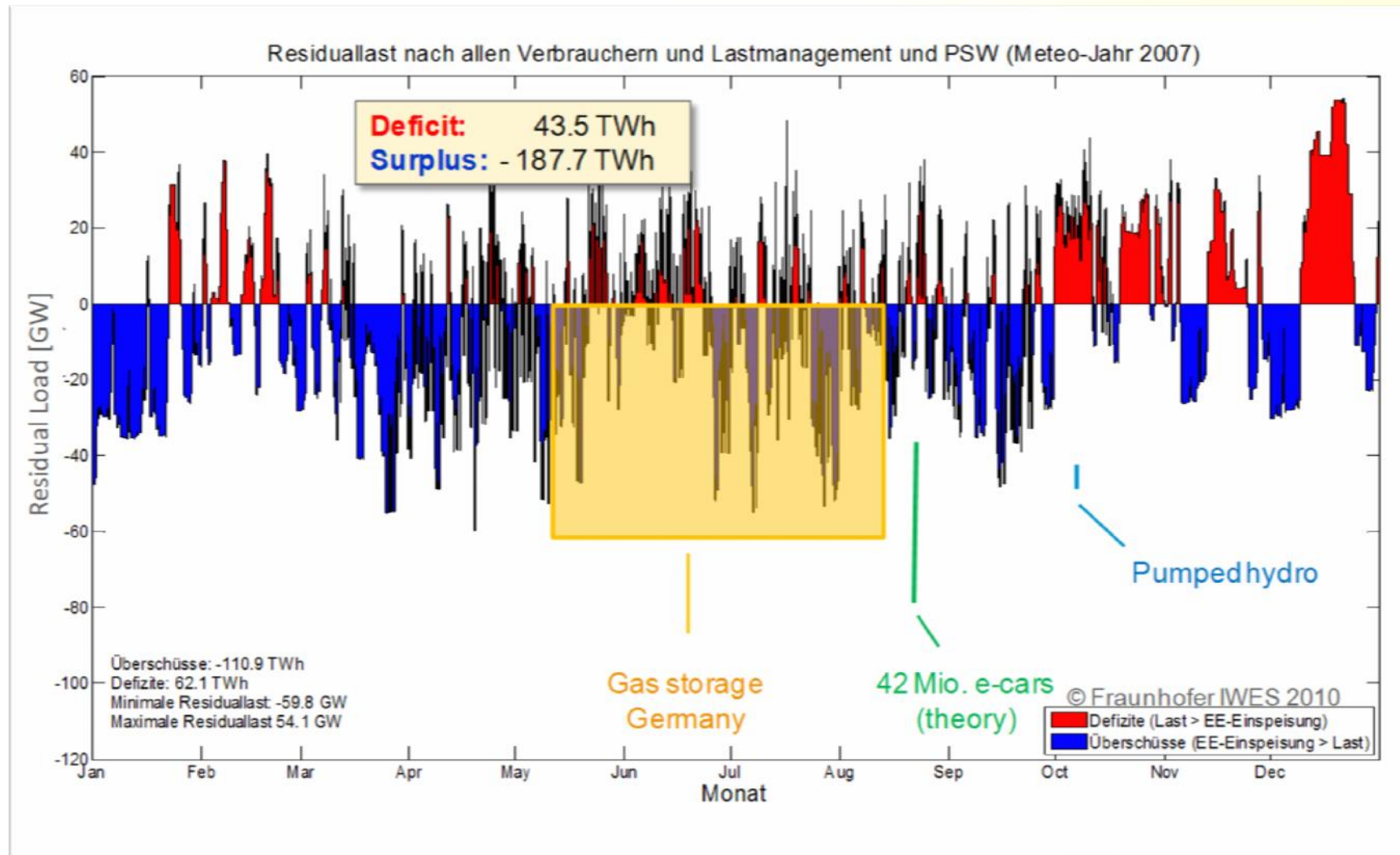
Project partners: DTU

- 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



Motivation

- Unique feature of storing energy as a chemical

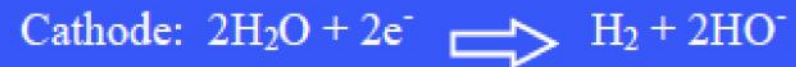
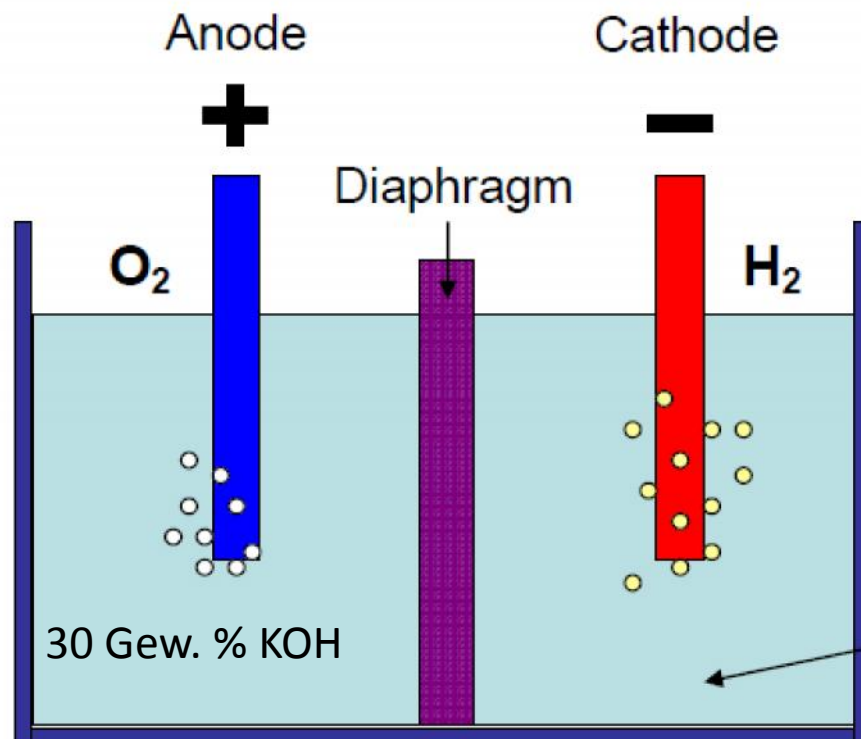


Motivation

- 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 H₂ fueling
- Higher efficiency without lowering output
 - Coatings
 - Cost/performance – business modelling

Motivation

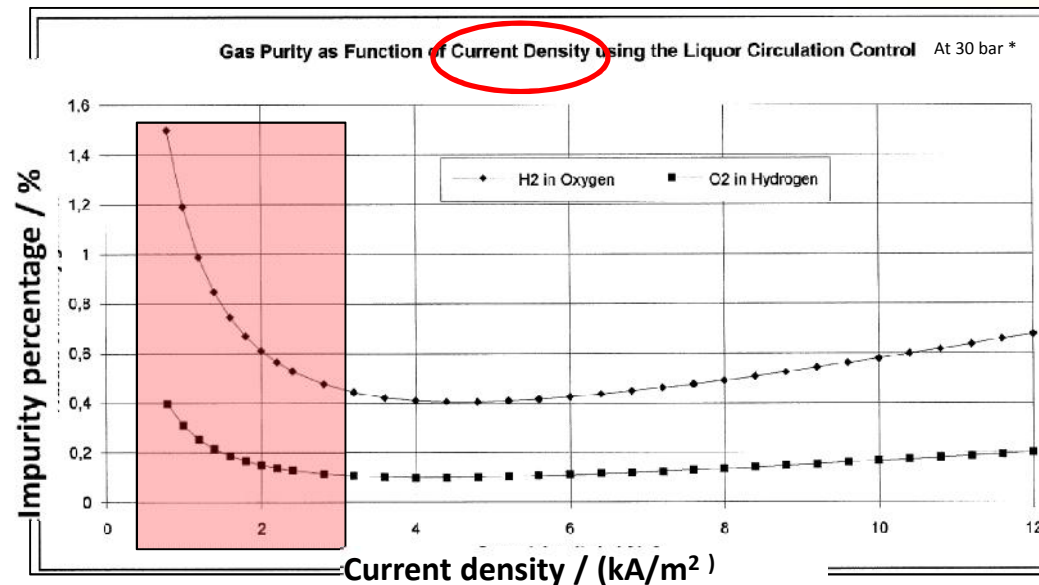
Alkaline water electrolysis



- 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 H₂ impurity in oxygen at low power and high pressure → safety problem
anode gas



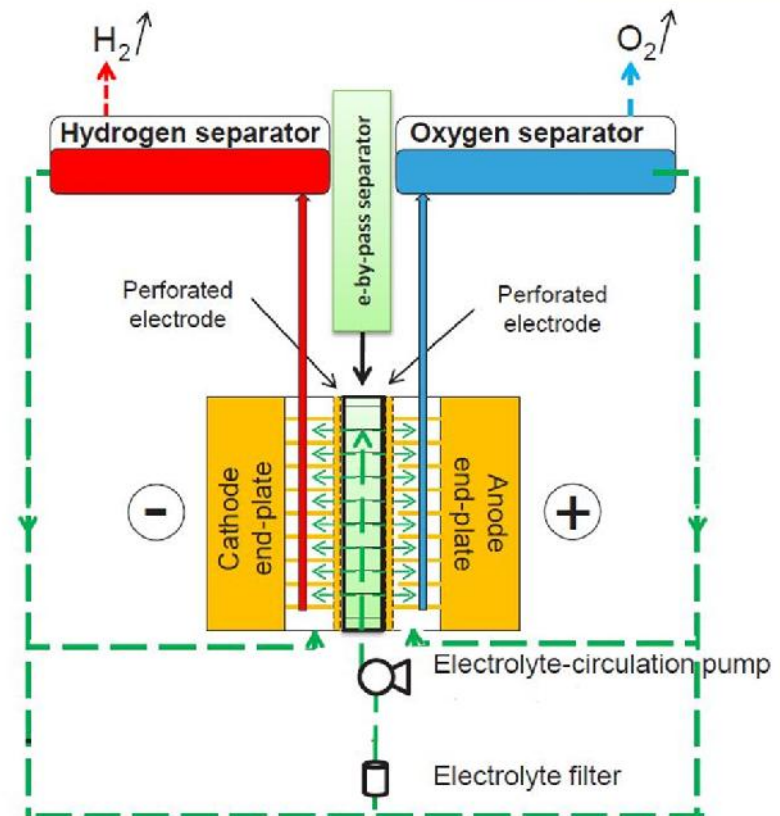
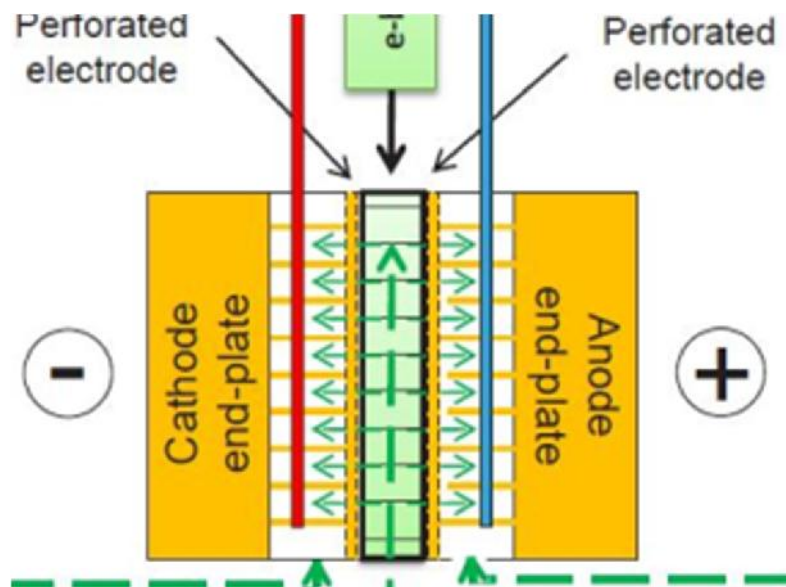
* C.A. Schug, Int J. Hydrogen Energy
23 (12) (1998) 1113

Reason for the problem:

- Diffusion of H₂ in O₂ and O₂ in H₂ dissolved in electrolyte depending on T, p
- At low current density and at high pressure H₂ to O₂ 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“

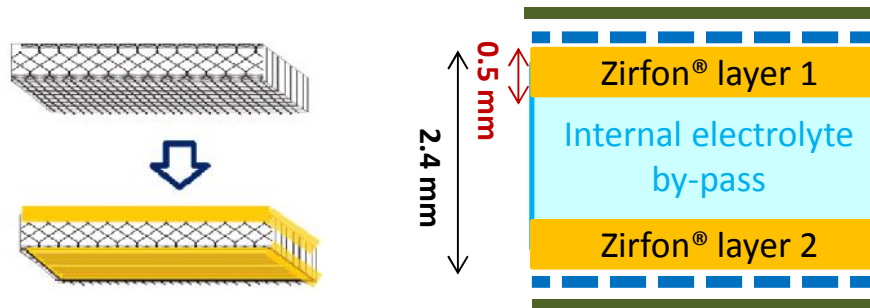
Goals: develop the “E-by-pass separator” diaphragm with internal electrolyte bypass

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[®] (ZrO₂/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 m² bar) to 900 l/(h m² bar)



Project approach: „E-by-pass separator“

Progress achieved:

- Separator of 300 cm² delivered for cell and stack integration
- Technical scale (2500 cm²) producibility demonstrated; relevant physico-chemical properties (R, Lp, BP) maintained upon upscaling

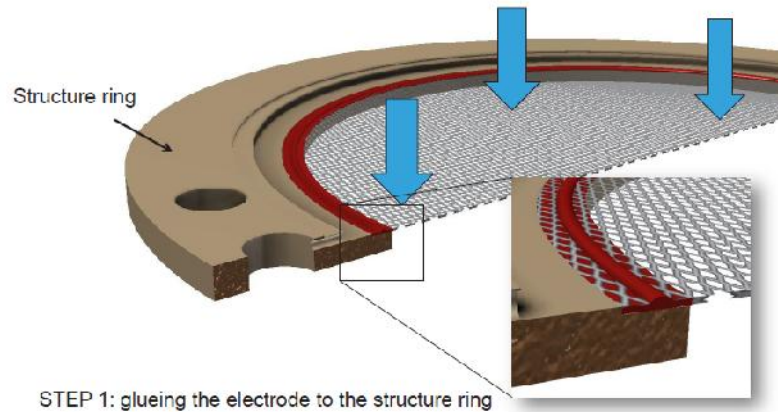


Project approach: „E-by-pass separator“

Cell construction integrating the e-by-pass separator –

Concept 1 Glue concept

Glueing of the membrane and electrode to the structure ring

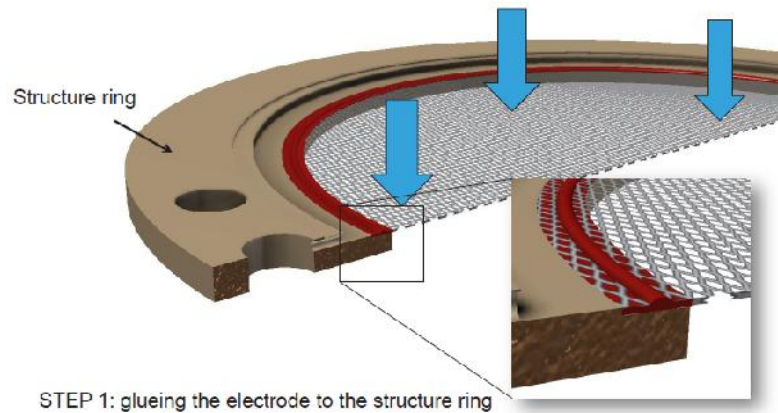


Project approach: „E-by-pass separator“

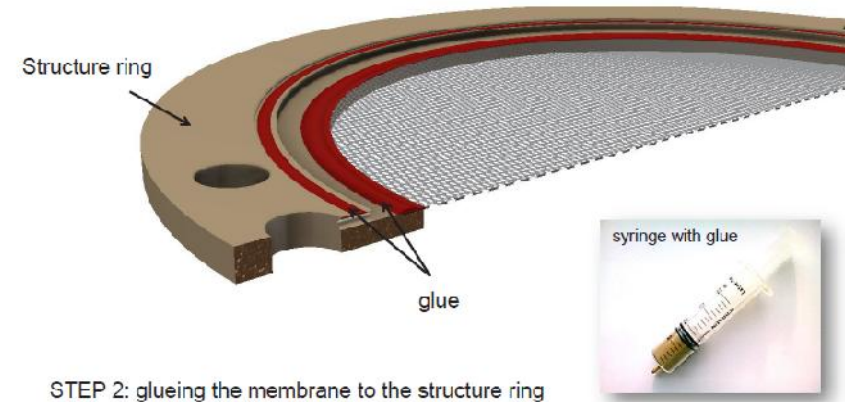
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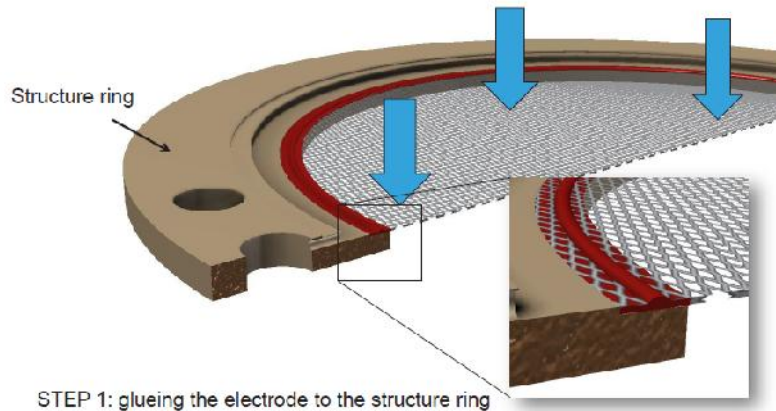


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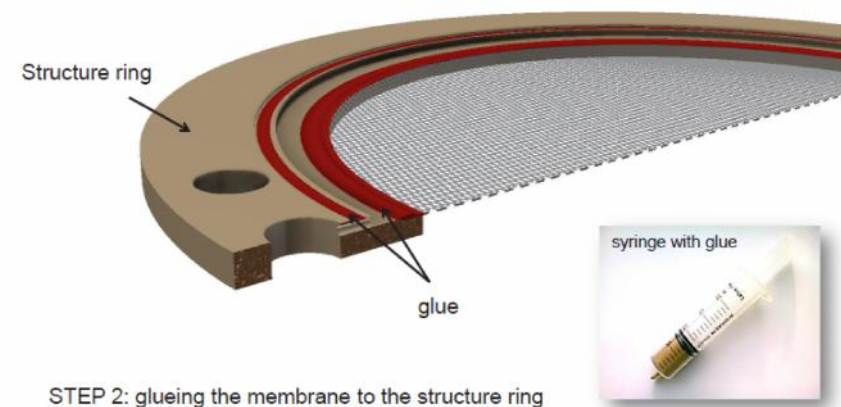
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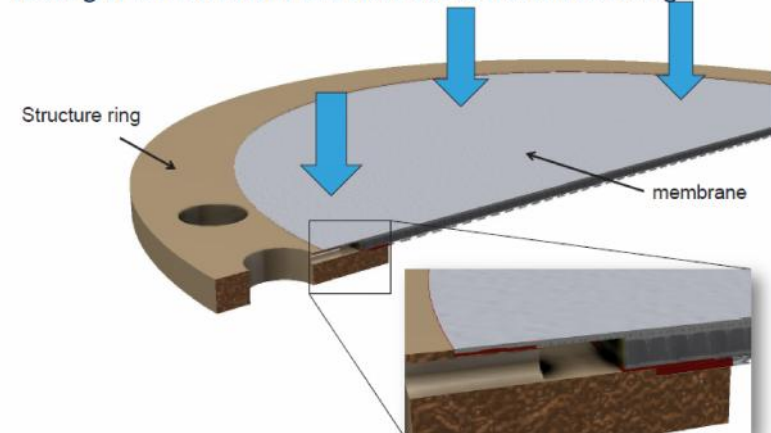
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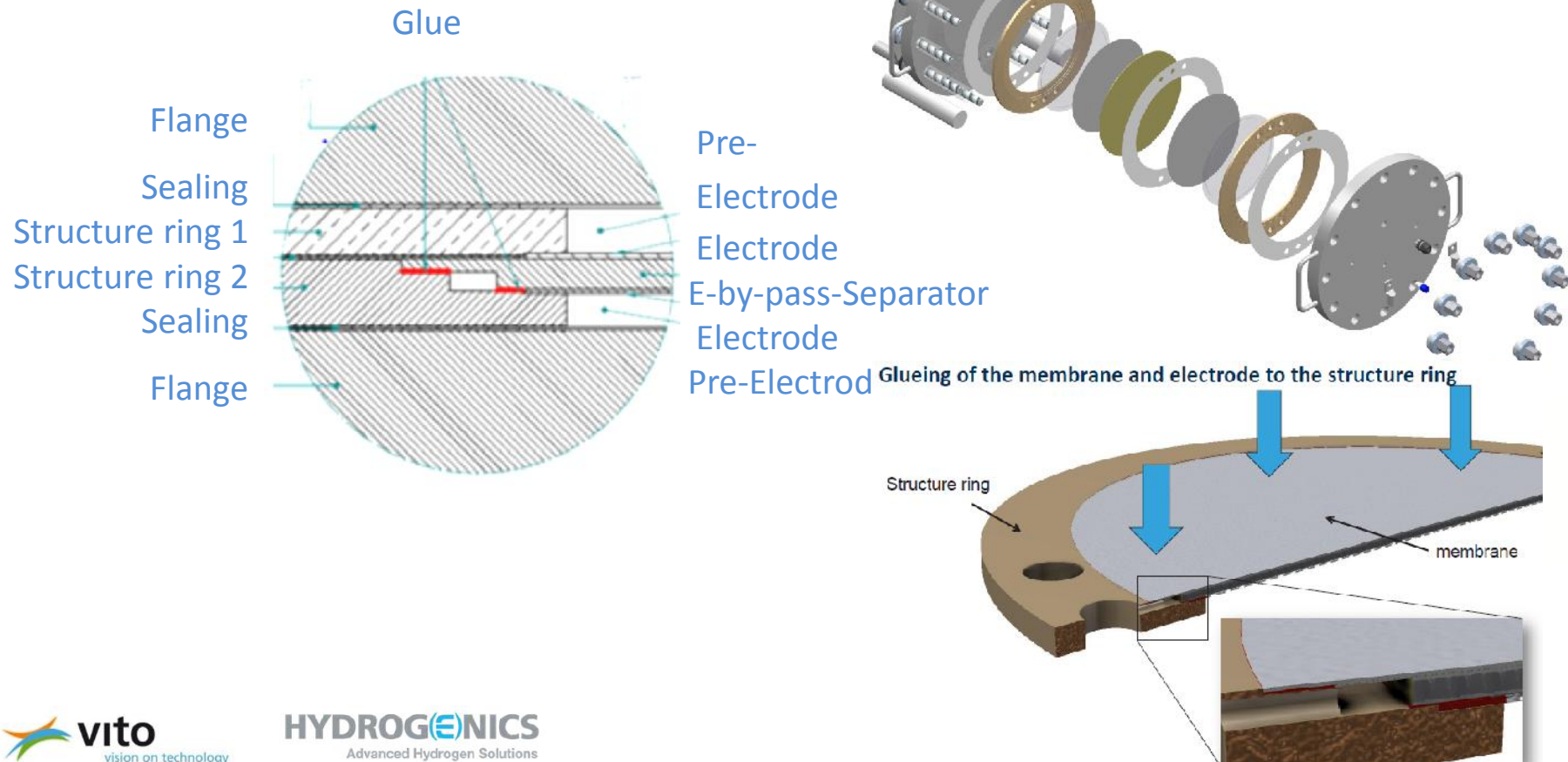


Glueing of the membrane and electrode to the structure ring



Project approach: „E-by-pass separator“

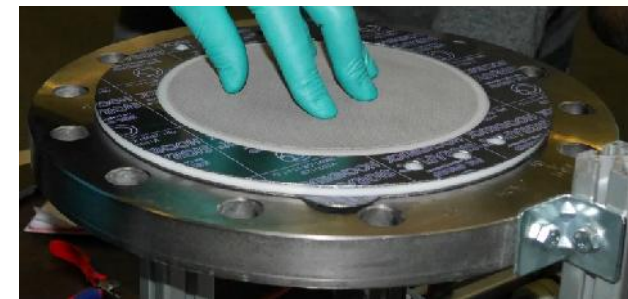
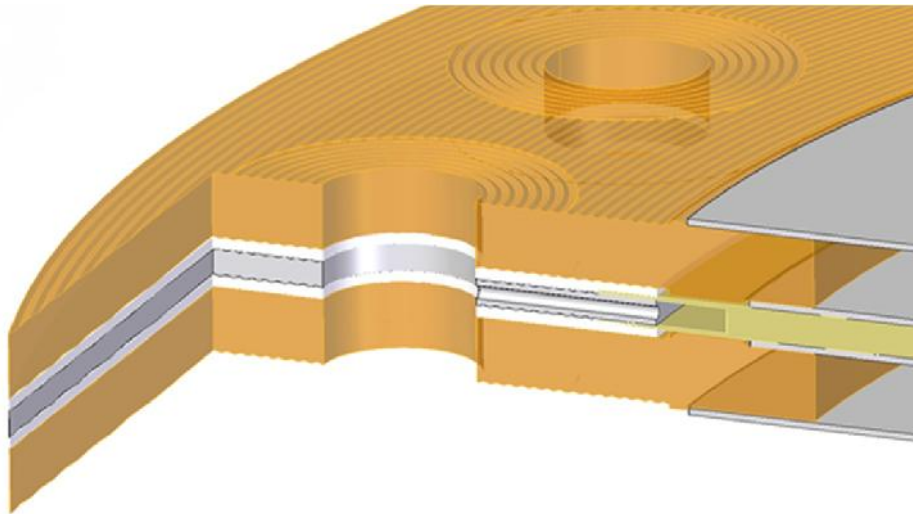
Cell construction integrating the e-by-pass separator – Concept 1 Glue concept





Project approach: „E-by-pass separator“

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



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 impurities (mostly from lye or separator)
- Deposition of metals (e.g. Fe),

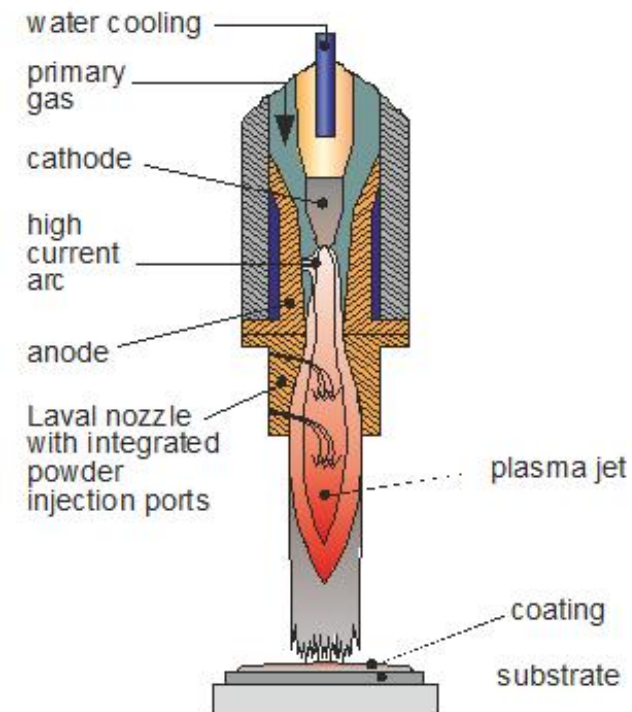
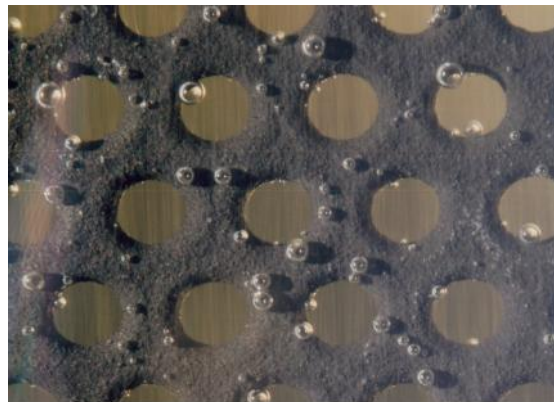
Better results using:

- 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

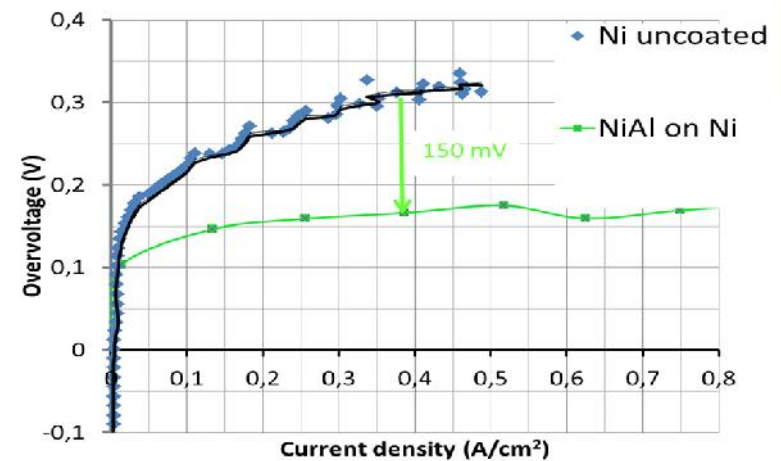
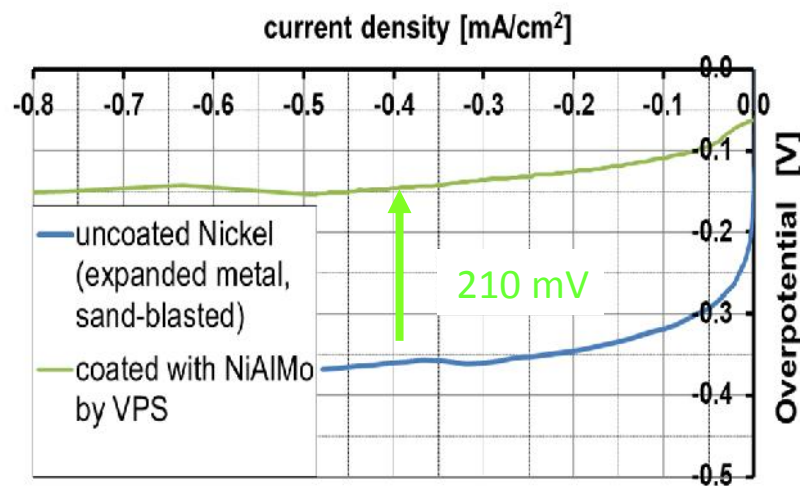
Electrode development for low overpotential, long life-time and low costs

Progress achieved:

Overpotential reduction to uncoated Ni electrode:

Cathode 210 mV using NiAlMo coating

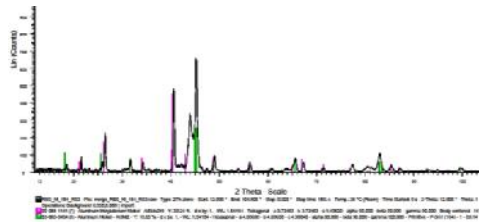
Anode 150 mV for NiAl



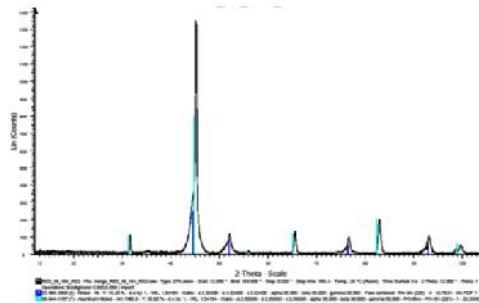
Project approach: VPS Raney Ni coating

Al is removed by leaching, high Ni surfaces are opened

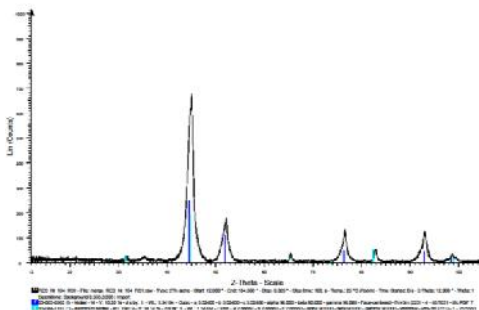
XRD metal phase composition:



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

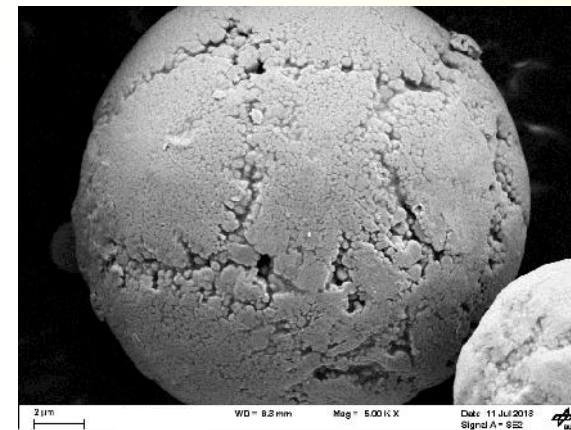


Leached at
80°C: still clear
NiAl signal

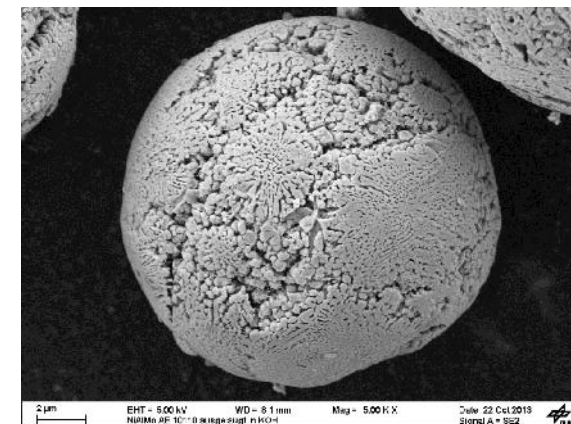


Leached at 90°C:
mostly Ni

SEM image original powder



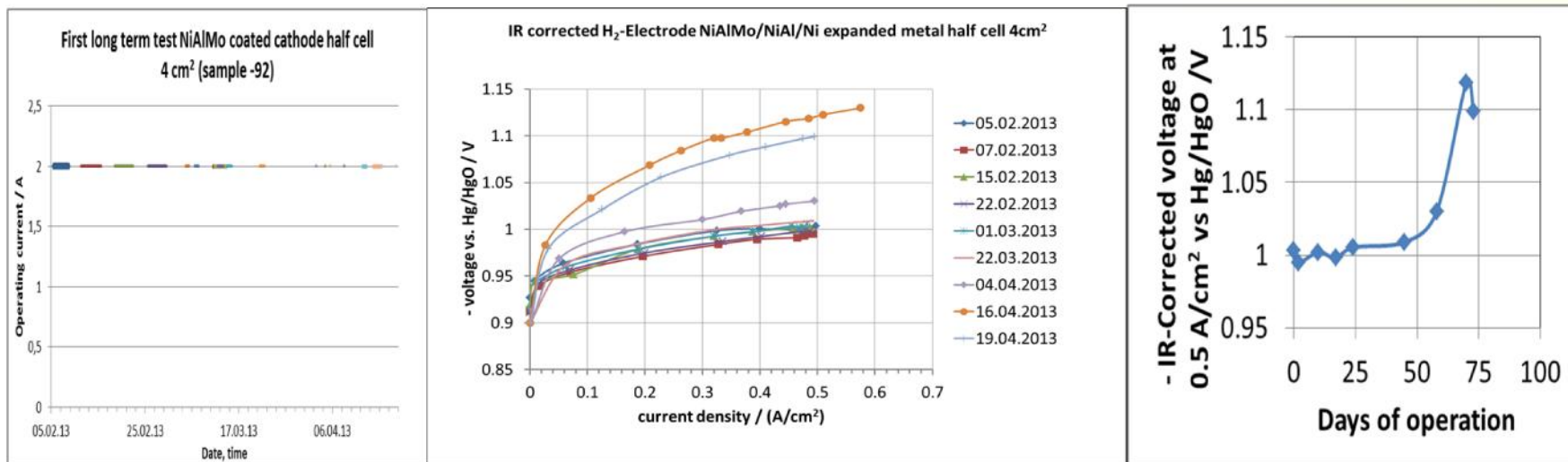
SEM image leached, activated powder:



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)

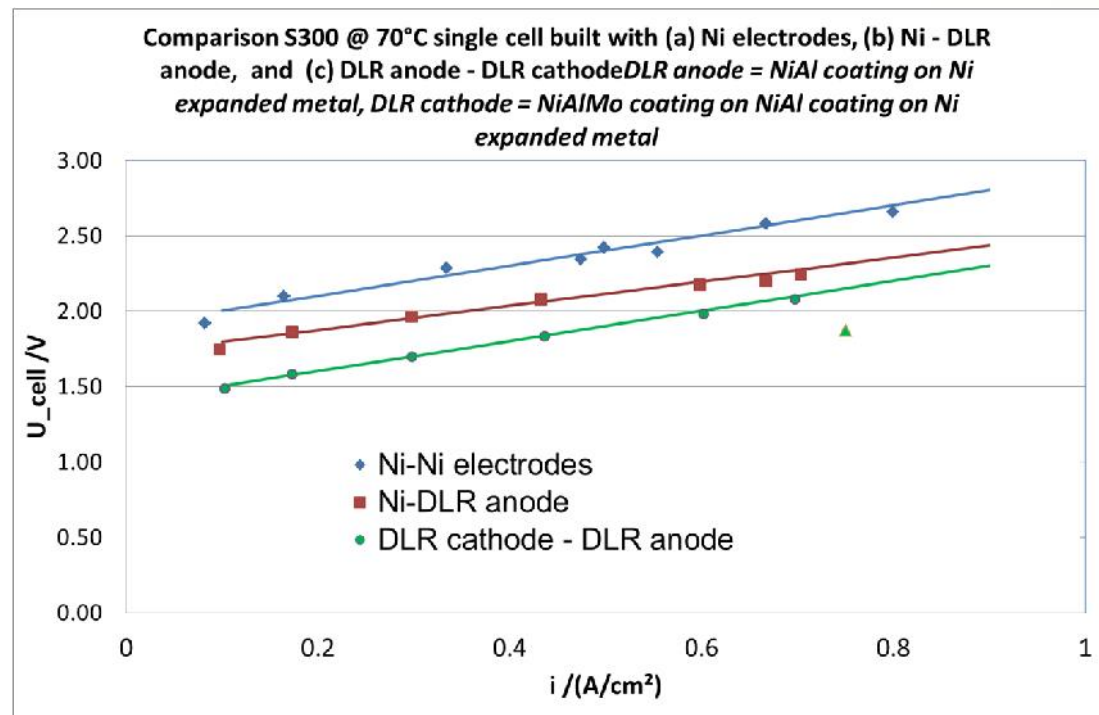


Improved by changing plasma spray parameters

Project approach: VPS Raney Ni coating

Full cell test 300 cm²:

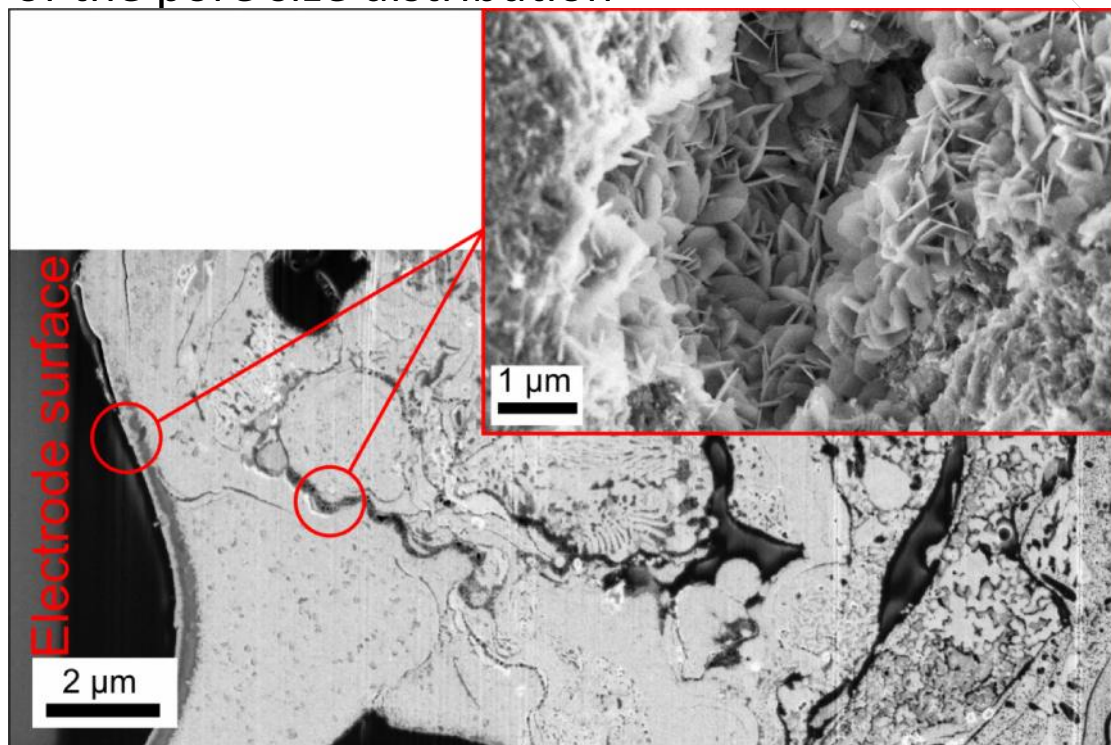
serious efficiency improvement when going from uncoated to coated electrodes.



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



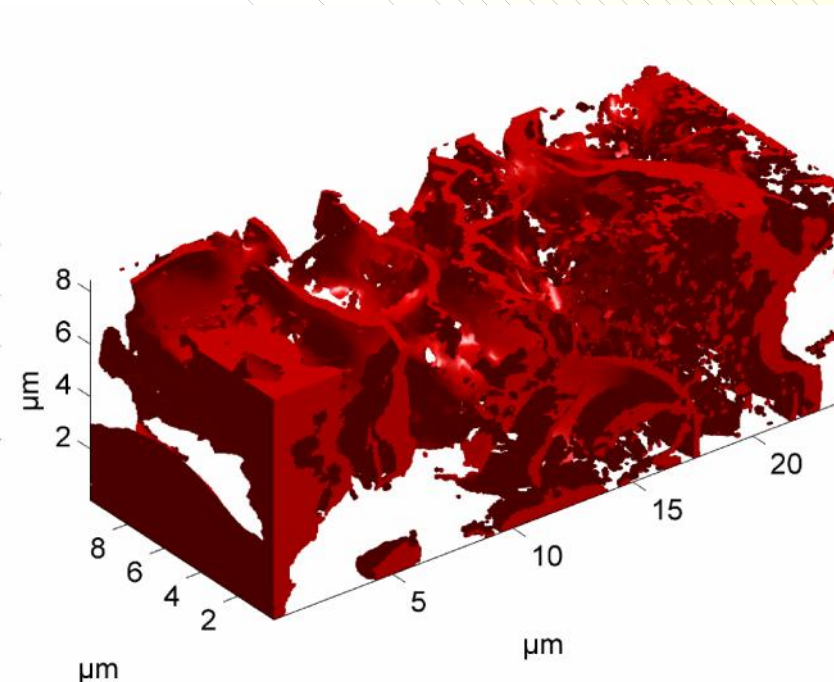
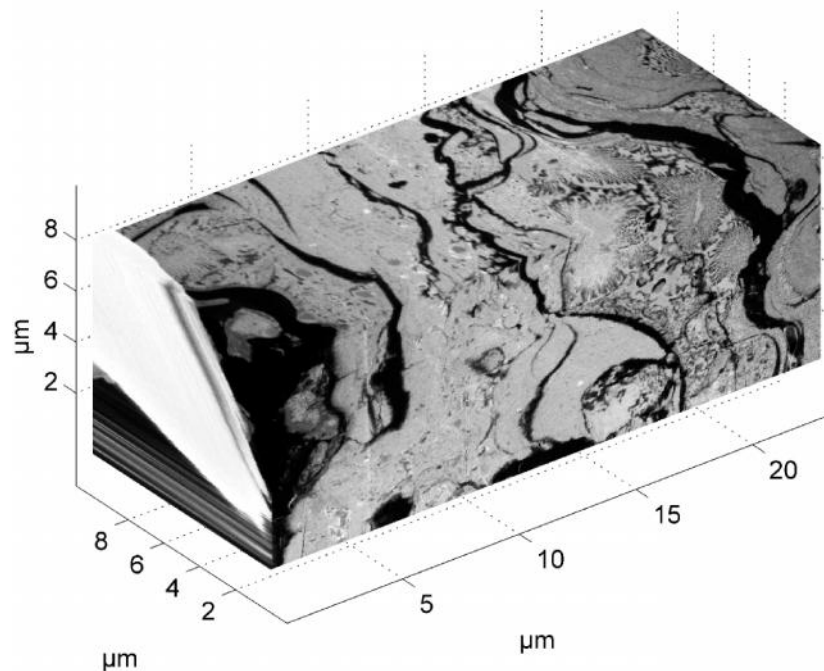
Electrode microstructure

- 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.



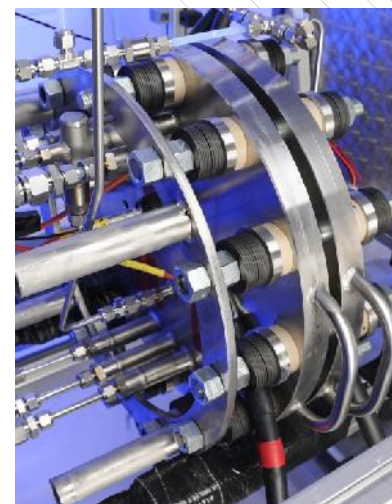
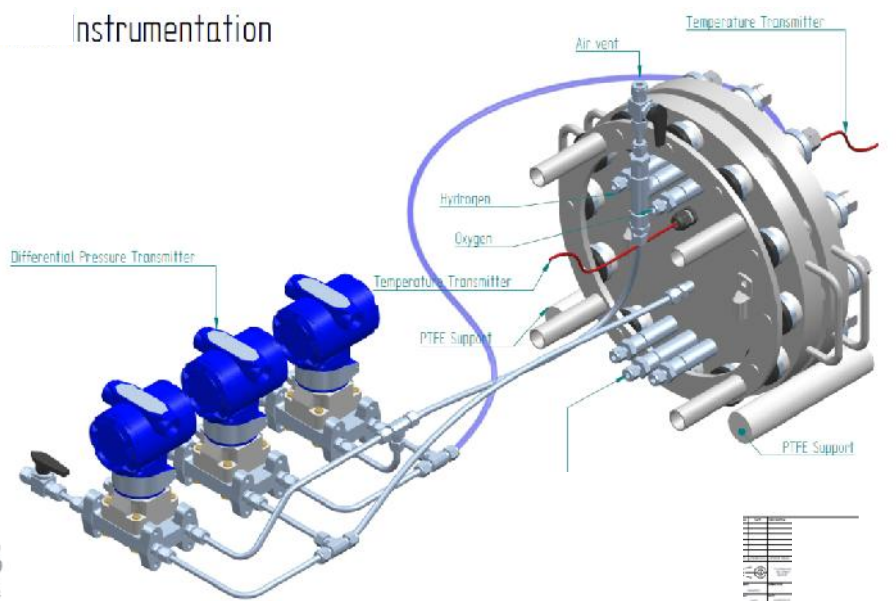


Cell and Stack Construction

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

Goal: realisation of electrolyzers 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





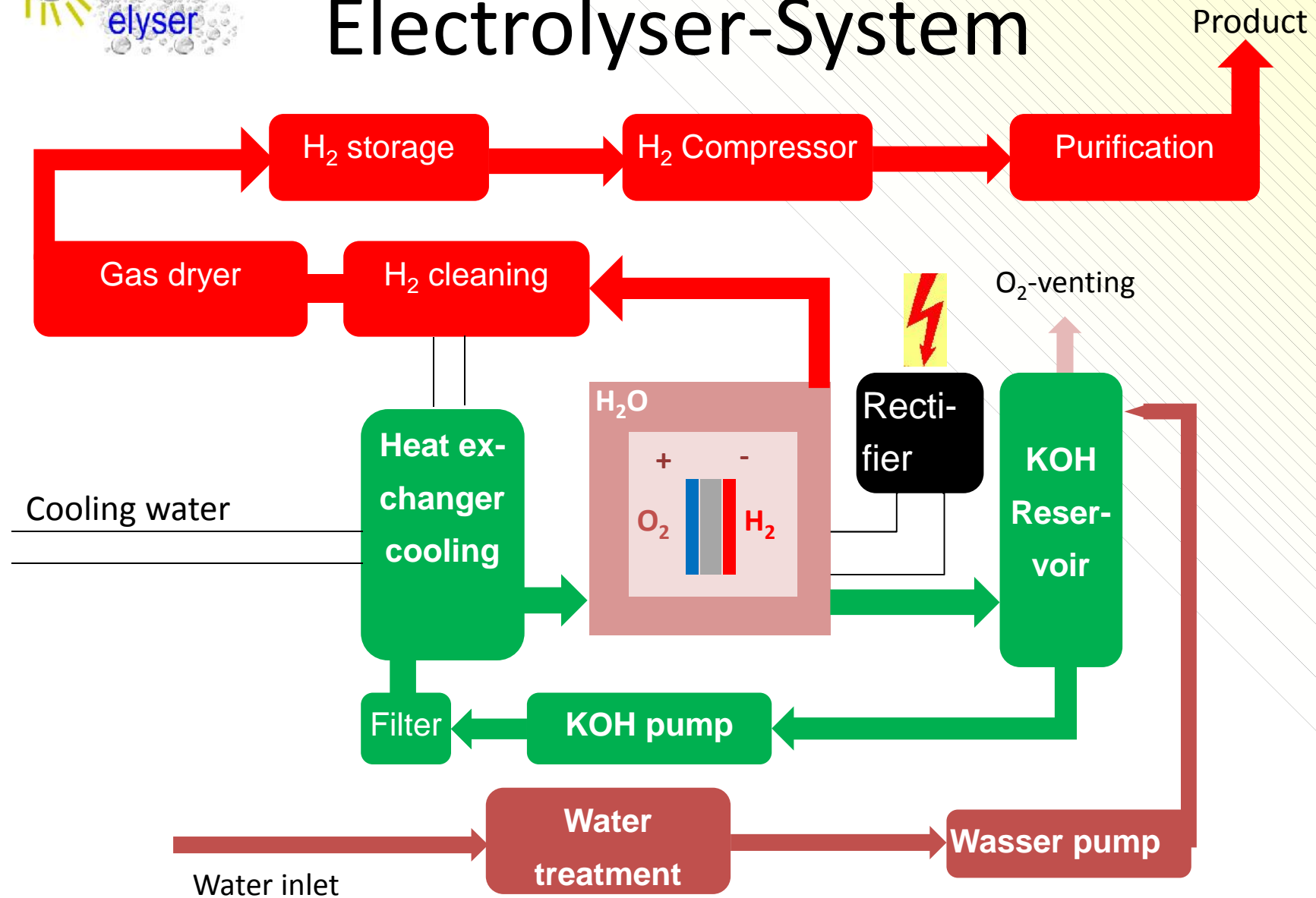
Cell and Stack Construction

- 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





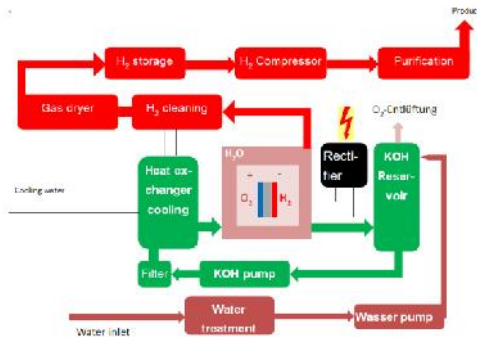
Electrolyser-System





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

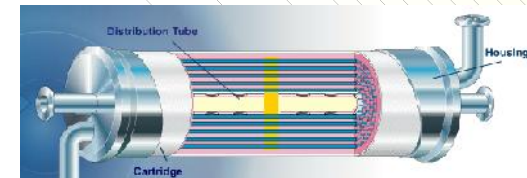
BOP and System

E-by-pass concept

needs additional electrolyte pump and electrolyte degassing
but no more H₂ 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 addresses some of the points to make alkaline electrolyzers 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 electrolyzers than what can be worked out in one project



Thank you for your attention

www.reselyser.eu

Regine Reissner

Deutsches Zentrum fuer Luft- und Raumfahrt

Regine.reissner@dlr.de



The end