Flexible Hybrid separation system for H_2 recovery from NG Grids

HyGrid

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Duration: 3 years. Starting date: 01-May-2016

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Introduction

- One of the main problems for the implementation of the hydrogen based economy is the transportation from production centers to the end user.

- One approach to solve this problem is to use the existing Natural Gas network for storing and distributing hydrogen.

The HyGrid technology will provide a route to:

- Increase the value of hydrogen blended into the natural gas grid, improving the economics of central hydrogen production from excess renewable energy couples with natural gas grid injection.

- Reduced cost, and therefore increased use of hydrogen from very dilute hydrogen streams in energy and transport applications.

- Further applications could be found in separating hydrogen from mixtures produced in chemical or biological processes, where it otherwise would be used to generate heat or even be vented.

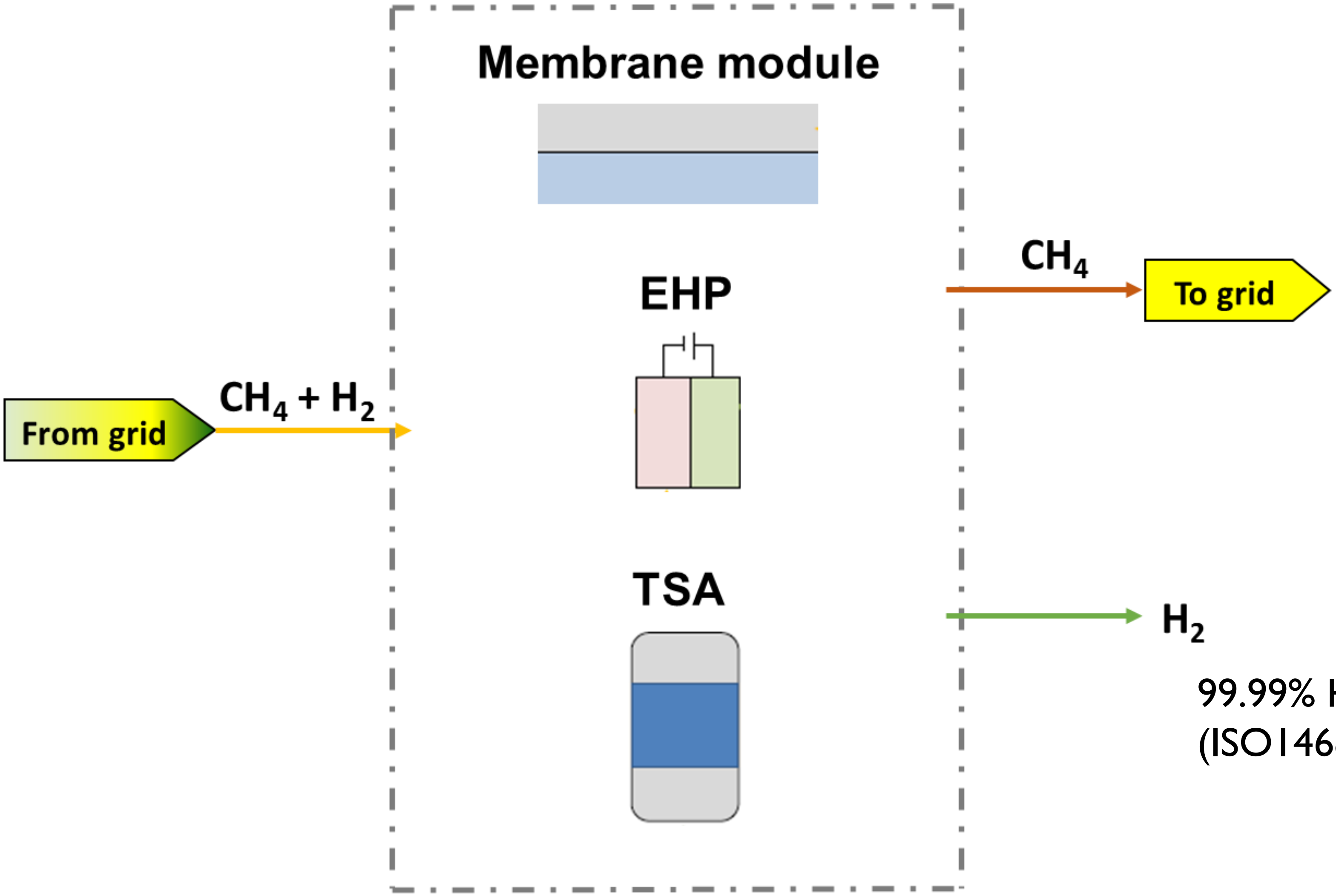
General concept

HyGrid **aims** at developing of an advanced **high performance**, cost effective separation technology for **direct separation of hydrogen from natural gas networks.**

The system will be based on:

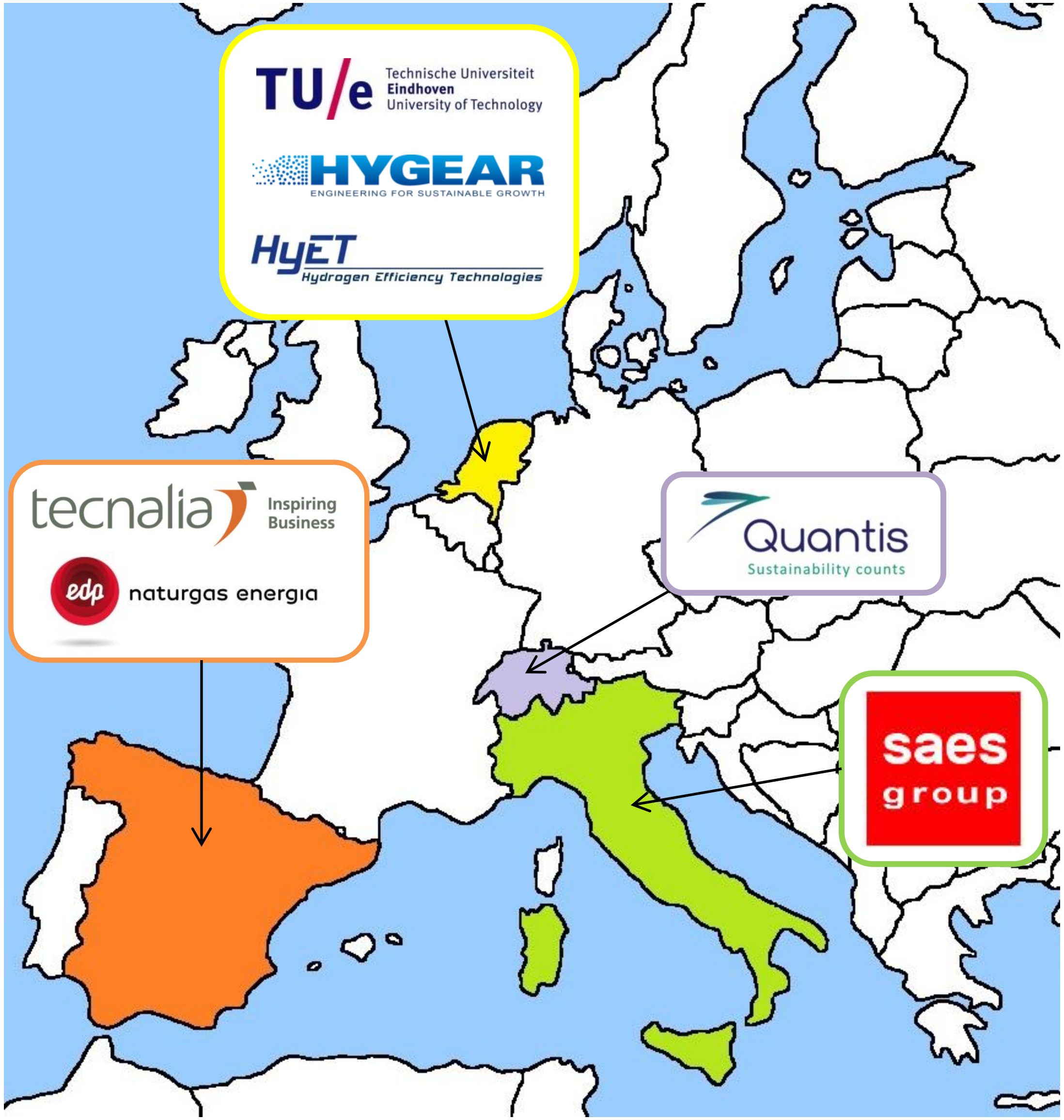
- Design, construction and testing of an **novel membrane based hybrid technology** for pure hydrogen production (ISO 14687) combining three technologies for hydrogen purification integrated in a way that enhances the strengths of each of them: **membrane separation technology** is employed for removing H2 from the "low H_2 content" (e.g. 2-10 %) followed by **electrochemical hydrogen separation** (EHP) optimal for the "very low H_2 content" (e.g. <2 %) and finally **temperature swing adsorption** (TSA) technology to purify from humidity produced in both systems upstream.
- The project targets a pure hydrogen separation system with **power** and **cost** of **< 5 kWh/kg$_{H2}$** and **< 1.5 €/kg$_{H2}$**. A pilot designed for **>25 kg/day** of hydrogen will be built and tested at industrially relevant conditions (TRL 5).

General concept



99.99% H_2 purity (ISO14687)

Partnership



Multidisciplinary and complementary team: 7 top level European organisations from 4 countries: 2 research institutes and 5 top industries (3 SME) in different sectors (from materials development to membrane modules and separation systems, etc.).

1 TU/e, Netherlands
2 TECNALIA, Spain
3 HYG, Netherlands
4 SAES, Italy
5 HYET, Netherlands
6 QUANTIS, Switzerland
7 EDP, Spain

Consortium

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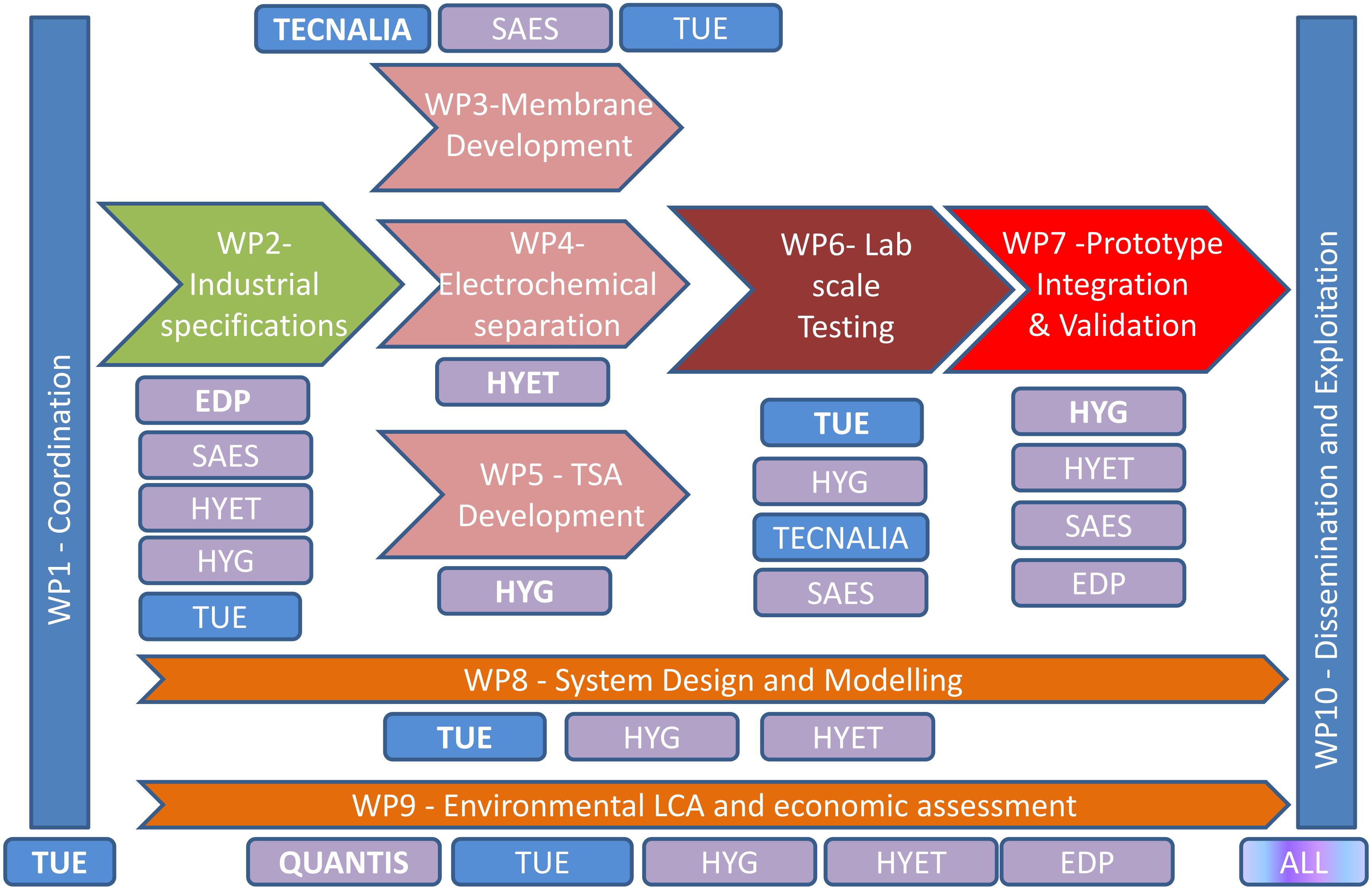
5 HYET, Netherlands
6 QUANTIS, Switzerland
7 EDP, Spain

Project objectives

- Development of a hydrogen separation system capable of targeting low (2-10%) and very low (<2%) H_2 blends in natural gas.
  - Membranes for H2 recovery from low hydrogen content streams (2-10%).
  - EHP for H_2 recovery from very low concentration streams (<2%) .
  - TSA for water removal from hydrogen/water streams.
- Technical validation of the novel modules at lab scale.
- Optimization of the hybrid system.
- Energy analysis of the new HyGrid technology on different scenarios:
  - recovery of H_2 from low concentration streams (2% -10%) up to 99.99% H_2 purity (ISO14687) in the whole range of pressures of the NG grid.
  - Different configurations/combinations of the three separation technologies
- The validation of the novel hybrid system at prototype scale (TLR 5)
- The environmental LCA of the complete chain.
- Dissemination and exploitation of the results.

Work Structure - Partnership Synergies



Membranes development

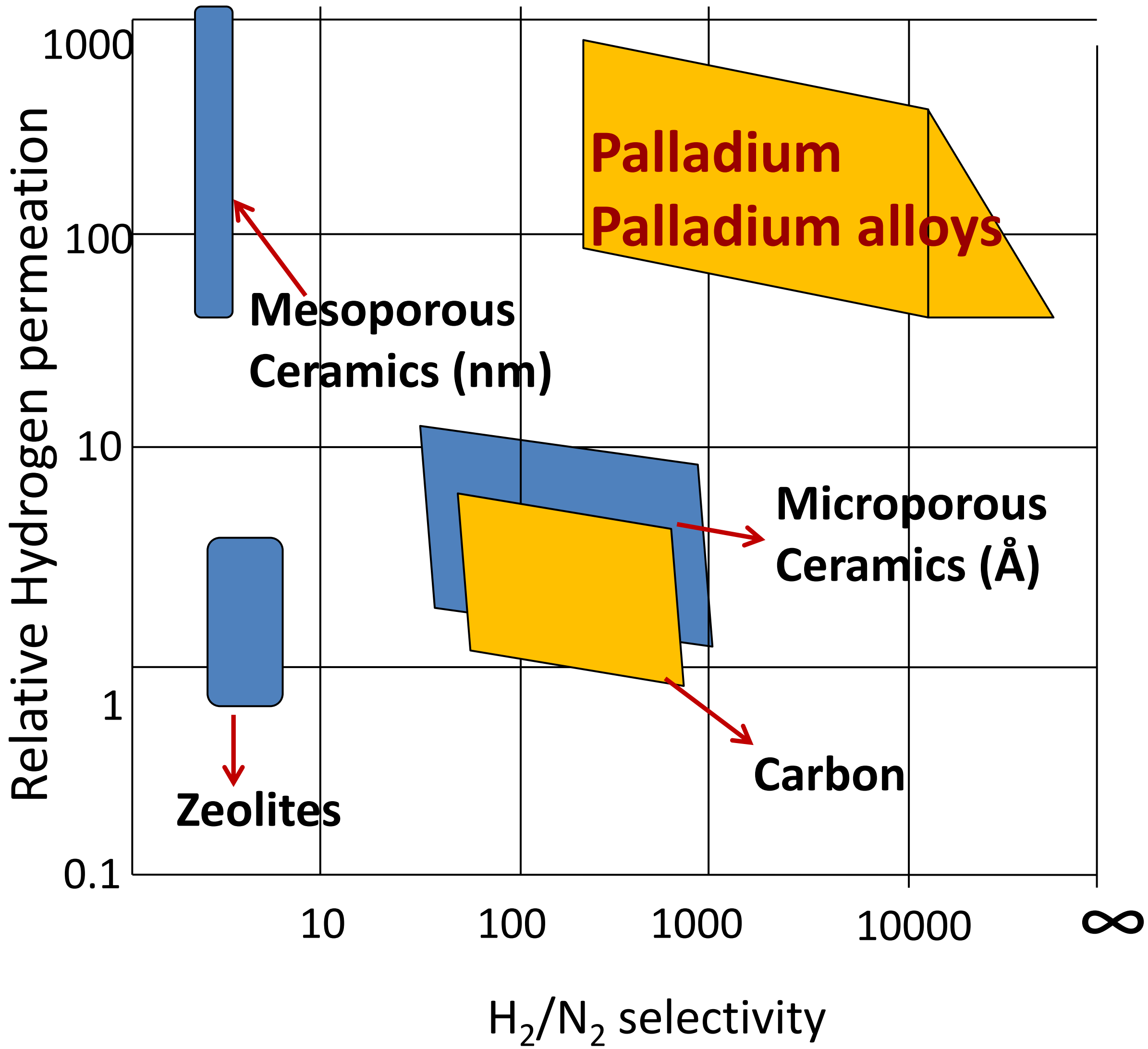
Objectives:

Development of cost effective tubular supported membranes for the recovery of hydrogen from low concentration streams (2% -10%) in the whole range of pressures of the Natural Gas Network. Two different types of membranes will be developed as well as the final membrane module:

- **Pd-based membranes** for the medium to the lowest Natural Gas Grid pressures with improved flux and selectivity.
- **Carbon Molecular Sieve membranes** for the high pressure range.
- Membrane **module for the prototype**.

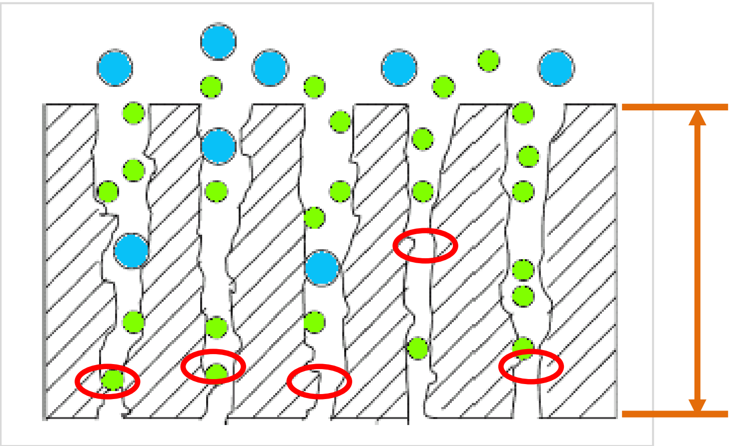
Inorganic, metallic & carbon membranes

Permation of H_2 against H_2/N_2 selectivity

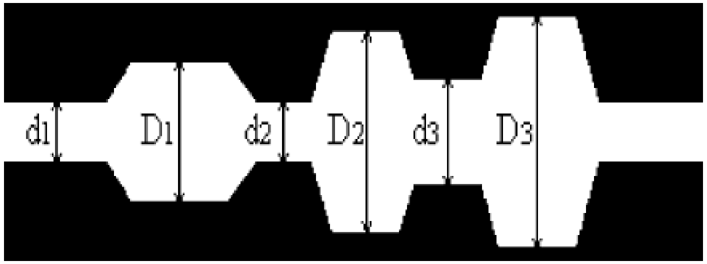


Carbon Molecular Sieve membranes

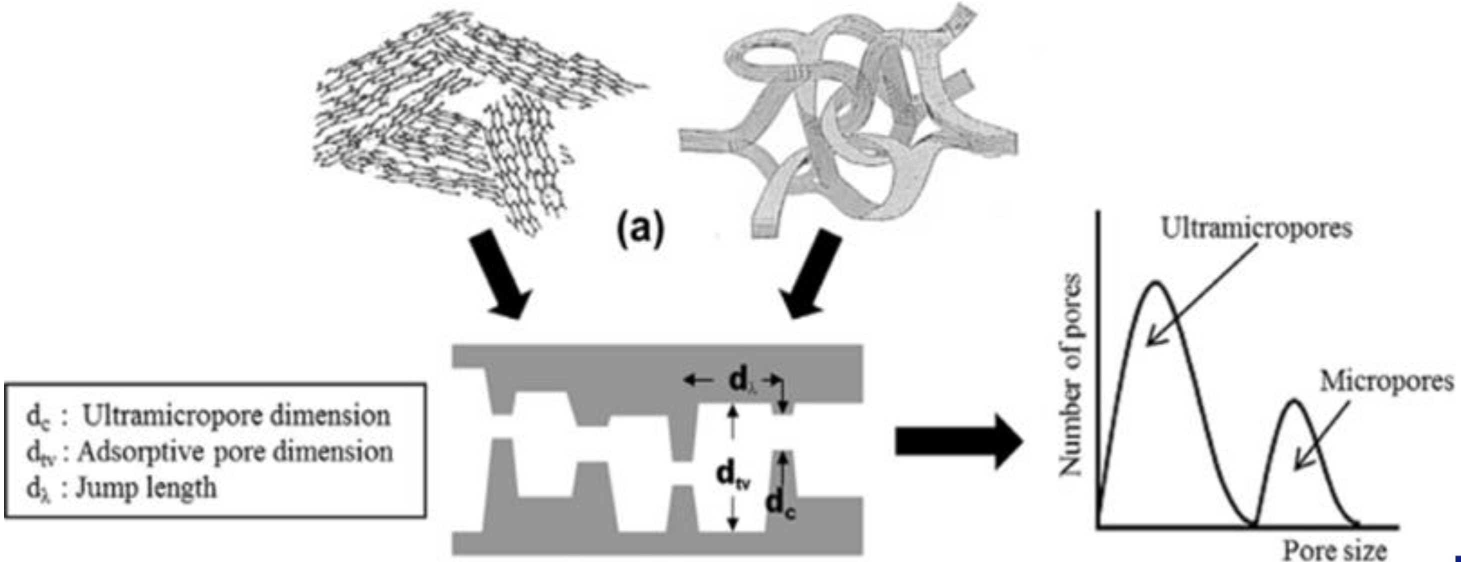
Transport mechanism



Membrane thickness

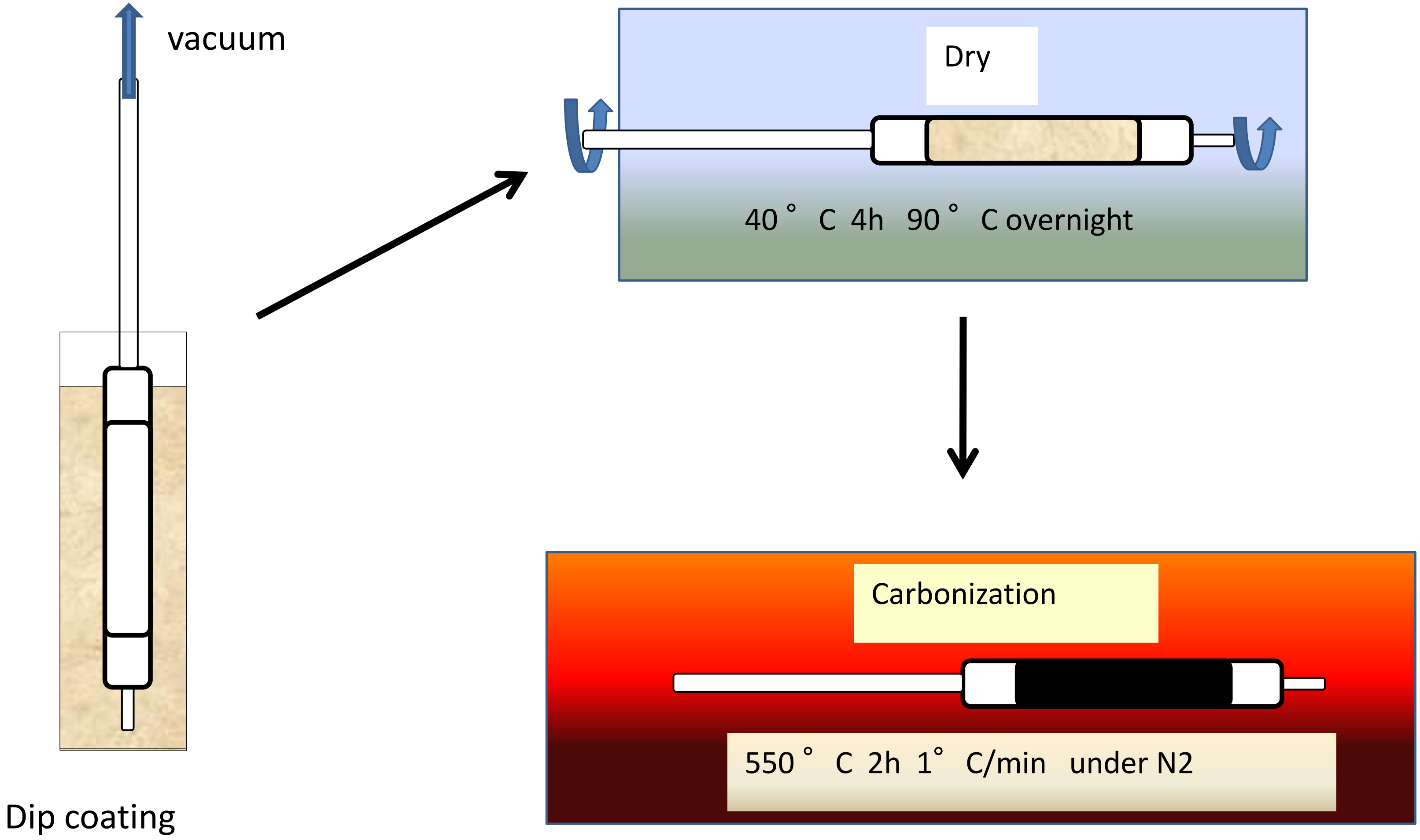


Nanopores + constrictions



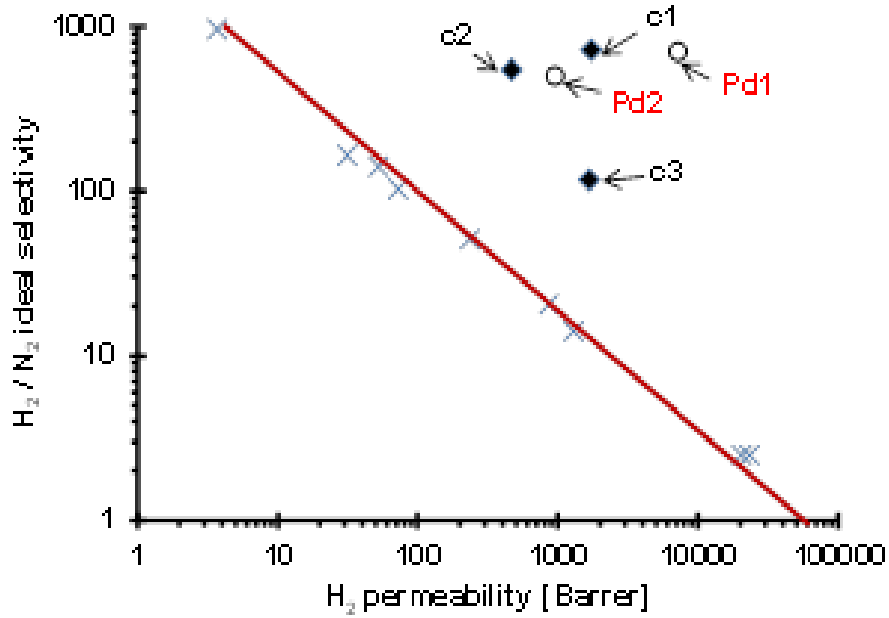
Carbon Molecular Sieve membranes

Preparation of composite Al2O3 – CMSM

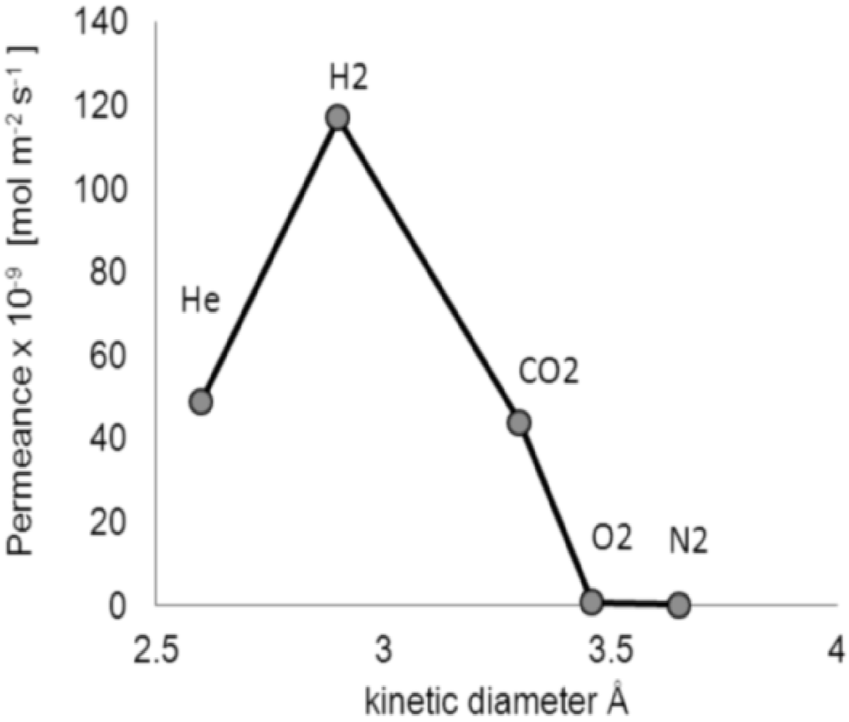


Carbon Molecular Sieve membranes

Robeson plot of the c-CMSM and Pd pore filled membranes



Gas permeation of composite Al-CMSM at 25 °C

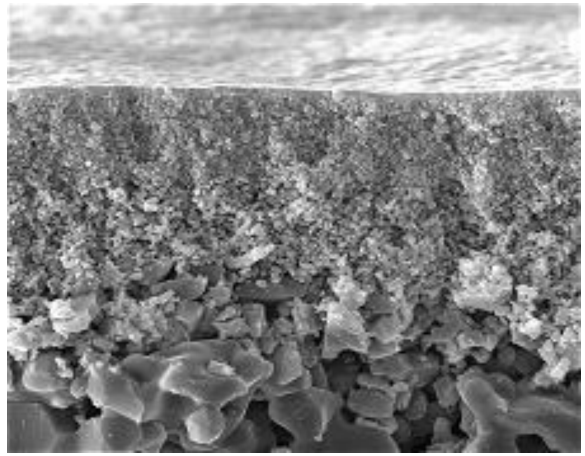


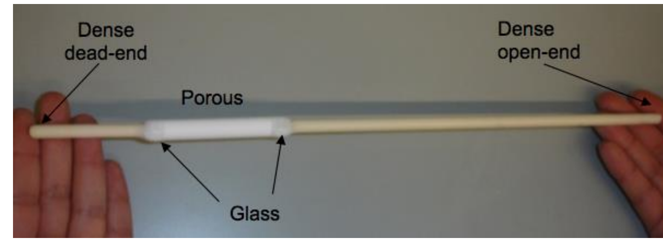
M.A. Llosa Tanco, D.A. Pacheco Tanaka, A. Mendes, Composite-alumina-carbon molecular sieve membranes prepared from novolac resin and boehmite. Part II: Effect of the carbonization temperature on the gas permeation properties, Int. J. Hydrogen Energy. 40 (2015) 3485–3496. doi:10.1016/j.ijhydene.2014.11.025

Ceramic supported Pd-based membrane

Porous Support:

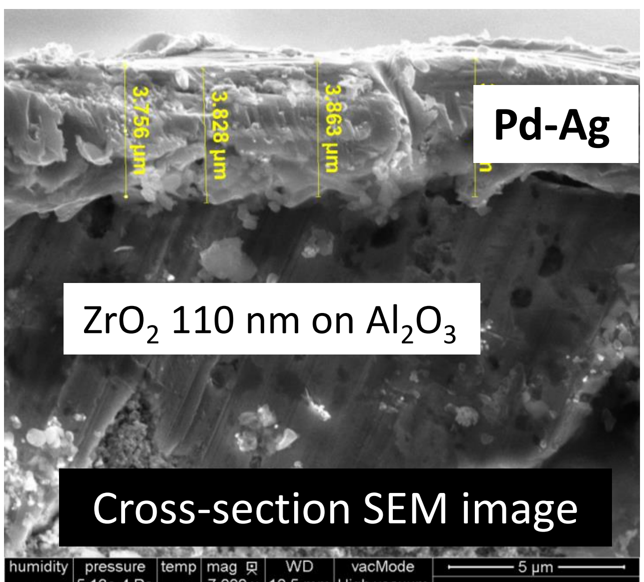
- Supplied by Rauschert
- 100nm pore size Al_2O_3





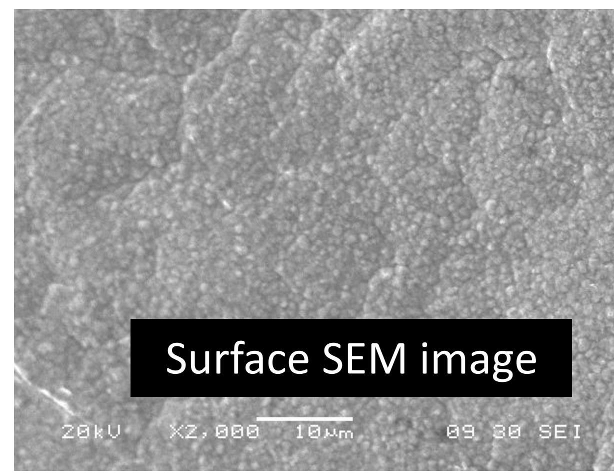
Join to dense ceramic tube at Tecnalia

Pd-Ag membrane layer deposition by Electroless Plating technique



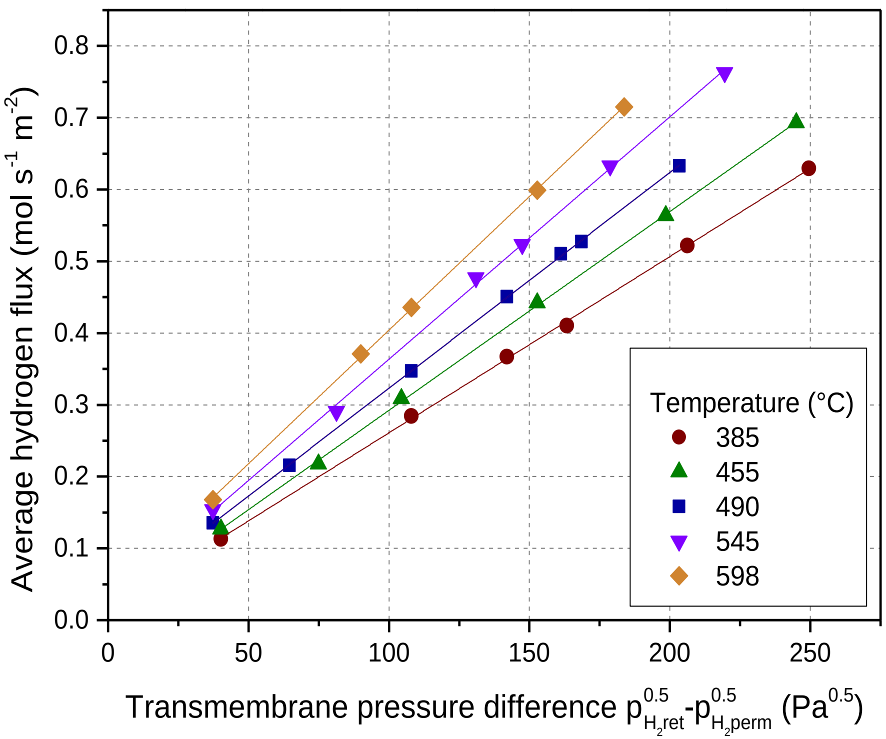
- ~4 µm thick Pd-Ag membrane
- Membrane length before sealing: 14-15 cm

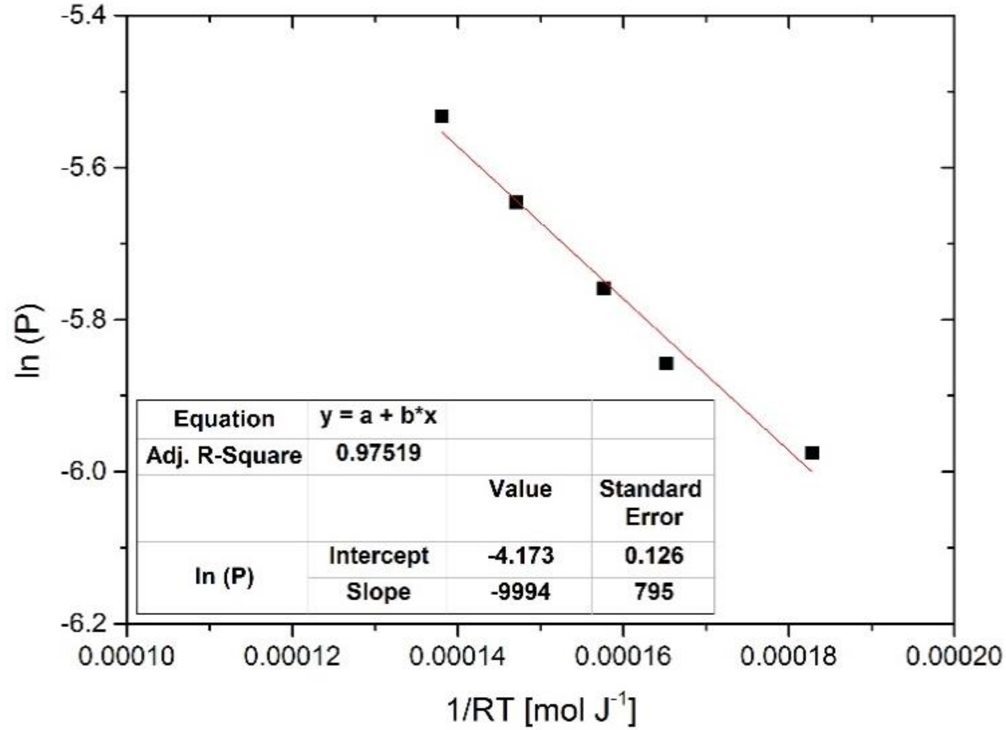
tecnalia Inspiring Business



Ceramic supported Pd-based membrane

Single gas permeation test



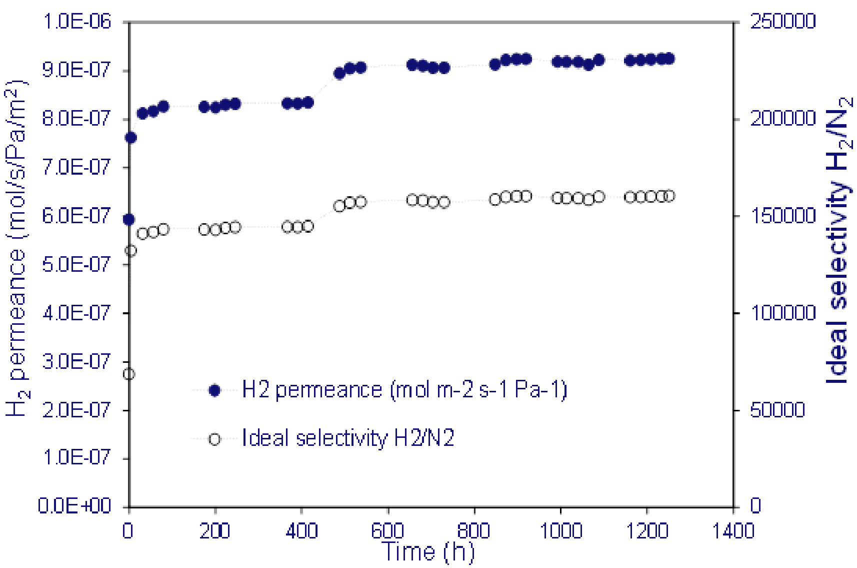


Ea: 10 kJ/mol; P^0: 6.93×10^{-8} mol m^{-1} s^{-1} $Pa^{-0.5}$

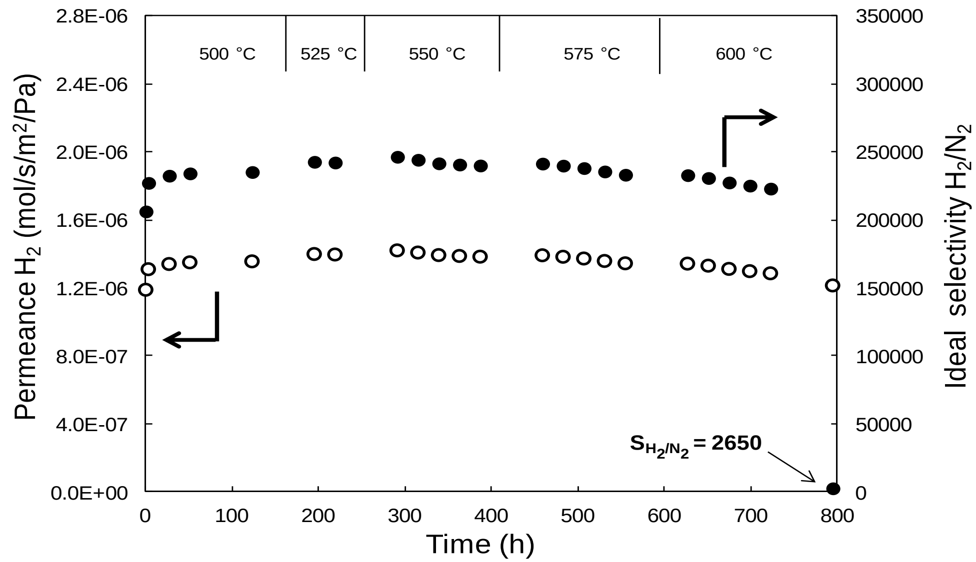
Fernandez et al., Preparation and characterization of thin-film Pd-Ag supported membranes for high-temperature applications. International Journal of Hydrogen Energy 40:13463-13478, 2015.

Metallic supported Pd-based membrane

Long-term stability test



Metallic supported membrane M14.
Long-term stability test over time at ***400 ºC***

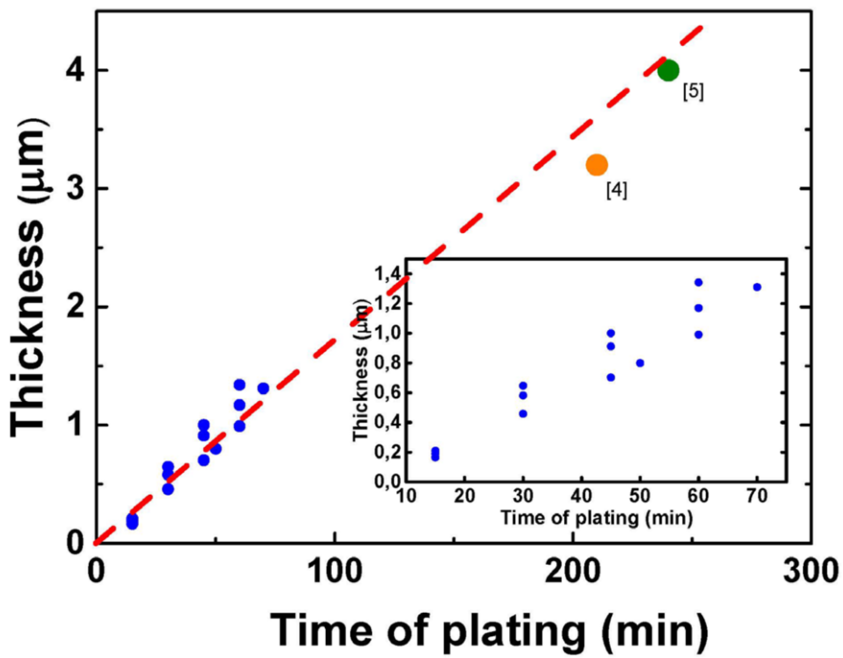


Membrane M17-E94.
Long-term stability test (**500-600 ºC**)

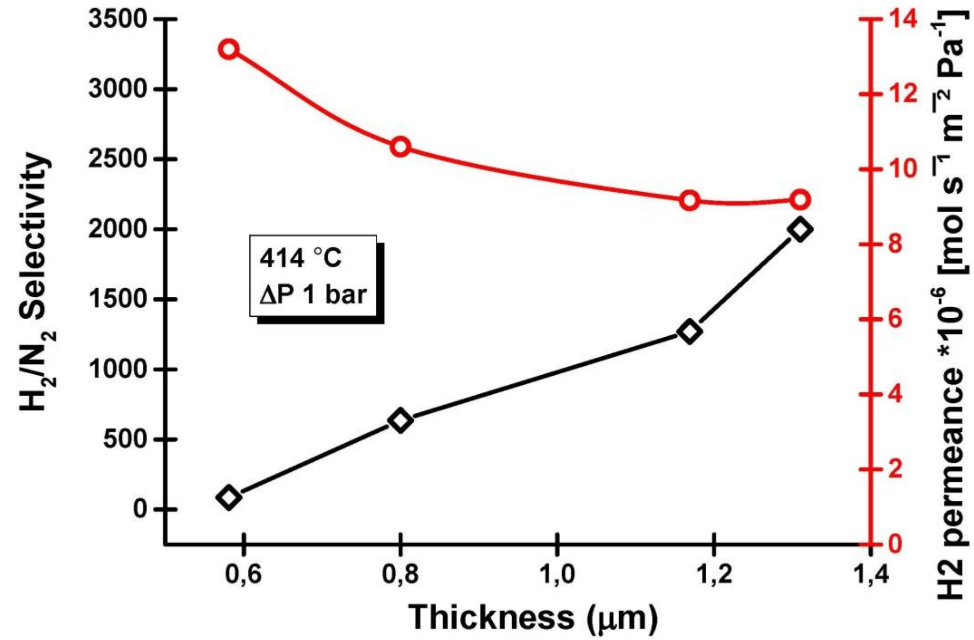
Medrano et al., Pd-based metallic supported membranes: high-temperature stability and fluidized bed reactor testing, International Journal of Hydrogen Energy, 2015. http://dx.doi.org/10.1016/j.ijhydene.2015.10.094

Ultra-thin (≈ 1 µm) supported Pd-Ag membranes by Electroless Plating

Thickness versus plating time



Selectivity and H_2 permeance versus thickness



- ● H_2 permeance (400°C)= 3.1x10^{-6} (mol m^{-2} s^{-1} Pa^{-1}); H_2/N_2= 8,000 – 10,000
- ● H_2 permeance (400°C)= 4.2x10^{-6} (mol m^{-2} s^{-1} Pa^{-1}); H_2/N_2= 20,000

- ➢ The thickness is controlled by the plating time
- ➢ There is a trade off between permeance and selectivity

FluidCELL FCH JU – FP7 project (www.fluidcell.eu)

Background on Pd-based membranes

Separation properties of membranes previously developed at TECNALIA

Membrane	Thickness	Porous support	H_2 permeance $\times 10^{-7}$ mol m^{-2} s^{-1} Pa^{-1} @ ΔP 1 atm	H_2/N_2 selectivity
Thin Pd-Ag	4-5 µm	Metallic	≈ 10 at 400 °C	>100.000
		Alumina*	≈ 30 at 400 °C	>20.000
Ultra-thin Pd-Ag	≈ 1 µm	Alumina	≈ 100 at 400 °C	> 2.000
CMSM	3-4 µm	Alumina	≈1 at 30°C	≈ 500

* Over DOE targets 2015

Permeation tests at gas compositions similar to the HyGrid (90% CH4 & 10% H2)

Membrane	Thickness	Porous support	H_2 permeance $\times 10^{-7}$ mol m^{-2} s^{-1} Pa^{-1} @ ΔP 1 atm	H_2/N_2 selectivity
Thin Pd-Ag	4-5 µm	Alumina	≈ 3,3 at 400 °C	>20.000
Ultra-thin Pd-Ag	≈ 1 µm	Alumina	≈ 11.8 at 400 °C	> 2.000

Electrochemical hydrogen separation development

Objectives:

Development of an electrochemical hydrogen purifier (EHP) for the recovery of the hydrogen from very low concentration streams (≤ 2 %).

- Capable of recovering the majority of the remaining hydrogen from the retentate of the membrane separator.
- Optimum configuration of membrane-electrode-assembly for low concentration hydrogen extraction.
- Theoretical modelling assisted optimum design of stack and gas distribution plate geometry for low concentration electrochemical hydrogen extraction (<3%).
- Construction and testing of sub- and full size electrochemical compressor stacks for model validation and prototype preparation.

Temperature Swing Adsorption development

Objectives:

Design, construction and test of the TSA unit.

- Better comprehension of the behaviour and performance of the adsorption materials used in TSA.
- Understanding of the response of adsorbents to the dynamic temperature control.
- Implementation of the know-how gained through lab tests onto the up-scaled design.
- Design of prototype TSA unit for integration in pilot scale HyGrid system.
- Testing of pilot scale TSA unit.

Lab scale testing

Objectives:

Design and test a small version of the prototype and test it at lab scale especially in conditions not feasible for the prototype.

- Investigate the recovery of the membrane system at different pressures and different concentrations of hydrogen.
- Sorbents for the TSA selected will be further studied in TGA experiments to evaluate the cyclic sorbent capacity and adsorption isotherms.
- Evaluation of different configurations to identify the optimum separation system along the natural gas network.

Prototype integration and validation

Objectives:

- Design of the integrated hydrogen recovery pilot plant
- Construct and assemble the hydrogen recovery pilot plant including controls
- Testing and assessment of hydrogen recovery pilot plant

System modelling and simulation

Objectives:

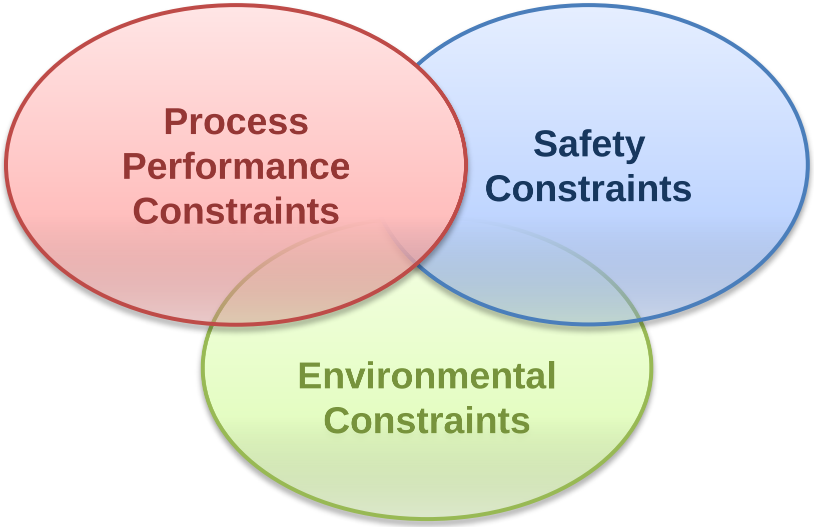
To assess the energy analysis, and economic performance (in terms of primary energy consumption and cost of pure H_2) of the HyGrid system for H_2 separation from NG grid.

- Membrane module model and simulation.
- Development of dynamic model for TSA.
- Modelling of electrochemical separation and compression.
- Simulation and economic optimization of integrated hydrogen recovery

Environmental LCA and economic assessment

The new H_2 separation technology will be analysed and compared to other available technologies using LCA and LCC in an iterative process to guide the design and development of the novel technologies and products towards sustainable solutions.

- An Environmental Life Cycle Assessment will be performed by applying and testing the most up-to-date life cycle impact assessment methods
- Life Cycle Costing will be performed and the latest advances in monetary valuation of impacts will be tested
- A business plan will be developed as part of the economic assessment



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HyGrid

Thank you for your attention

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