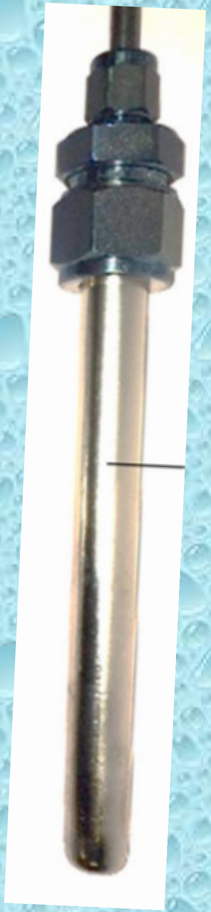
tecnalia

MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

TU/e Technische Universiteit Eindhoven University of Technology

Where innovation starts

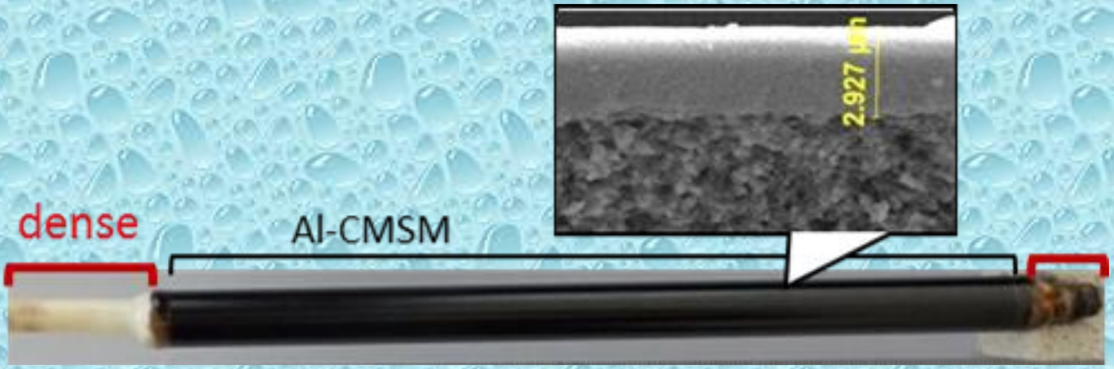


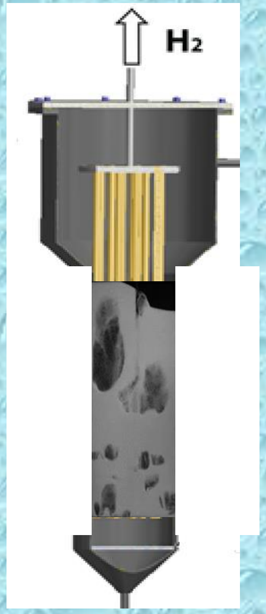
Tecnología de membranas para contrarrestar el calentamiento global

David Alfredo Pacheco Tanaka

Margot Llosa

Fausto Gallucci





Temas a tratar

- Membranas
- 7 separaciones que cambiarán el mundo
- Calentamiento global emisiones de CO_2
- Soluciones para evitar el calentamiento global
- Hidrógeno:
  - usos producción
  - separación membranas de paladio
  - Intensificación de procesos reactores de membrana
  - Hidrógeno verde
  - Almacenamiento y distribución
- Electrolizadores
- Amonia
- Valorización de CO_2

Programa para incorporación de investigadores

Contrato 06-2019-Fondecyt-BM-INC.INV

CONCYTEC

FONDECYT

FONDO NACIONAL DE DESARROLLO CIENTÍFICO, TECNOLÓGICO Y DE INNOVACIÓN TECNOLÓGICA

MEMTECH

UCSM Membranes For Water Purification

Uso de la nanotecnología en el desarrollo de membranas para Desalinización, purificación de aguas e industria alimentaria-

UNIVERSIDAD CATÓLICA DE SANTA MARÍA 1961

UNIVERSIDAD NACIONAL DEL ALTIPLANO PUNO

Holanda

TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY

Australia

IFM INSTITUTE FOR FRONTIER MATERIALS

DEAKIN UNIVERSITY

1 investigador principal

1 investigador asociado

2 Post-docs

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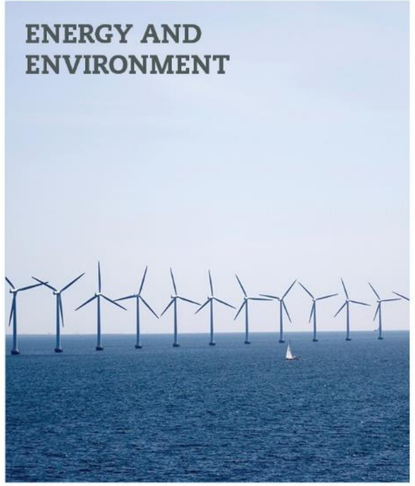
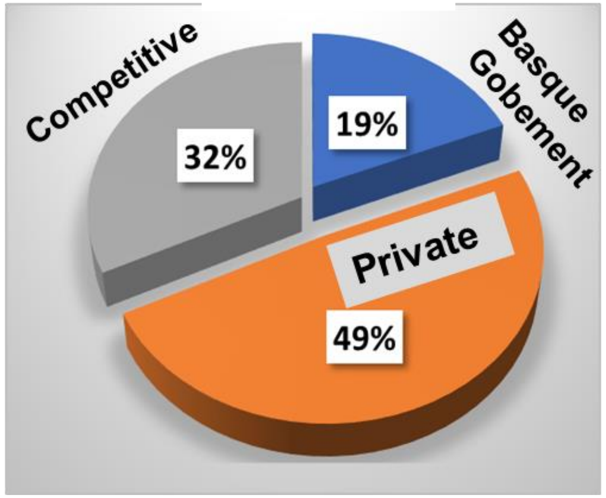
6 BUSINESS DIVISIONS



Staff 1407

Income 110 M €

Funding



European Commission
HORIZON 2020

228
Approved projects

TU/e Technische Universiteit Eindhoven University of Technology

Where innovation starts

Prof. Fausto Gallucci
Decano Facultad

DEPARTMENT

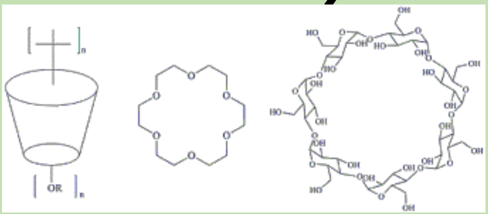
Chemical Engineering and Chemistry

GROUP

Inorganic Membranes and Membrane Reactors

UNIVERSITY OF SURREY

PhD Chemistry

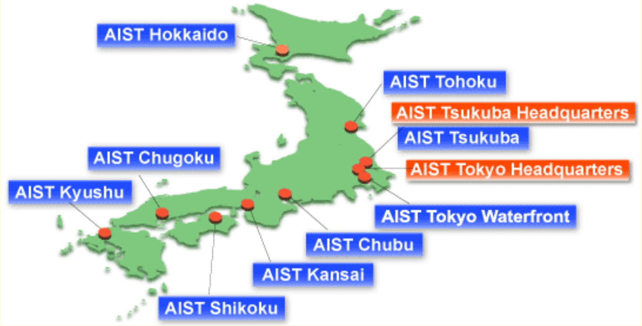


Supramolecular Chemistry

1991 - 1996

AIST NATIONAL INSTITUTE OF ADVANCED INDUSTRIAL SCIENCE AND TECHNOLOGY (AIST)

Japan



Removal and detection of toxic ions from water

Pd membranes for hydrogen separation

1997 - 2008

U.PORTO
FEUP FACULDADE DE ENGENHARIA UNIVERSIDADE DO PORTO

Carbon membranes
Fuel cells
Photocatalysts
Solar Cells
Graphene

2008- 2012

tecnalia Inspiring Business

Carbon membranes
Pd membranes
Process intensification
Water desalination

2012- now

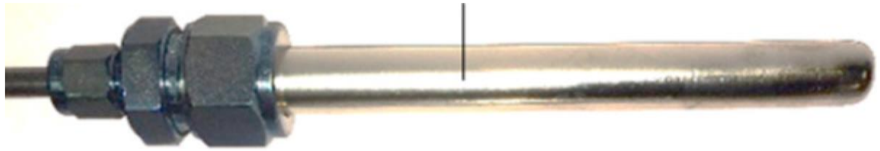
TU/e Technische Universiteit Eindhoven University of Technology
Where innovation starts

The Netherlands

¿Qué es una membrana?

Es un medio solido o líquido cuyas dimensiones laterales son mucho mayores que su grosor y que sirve *como barrera selectiva* entre dos fases.

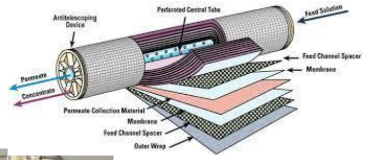
La diferencia en la resistencia al paso de diferentes moléculas proporciona la selectividad.



Diseño de módulos de membrana

[membrane surface to volume ratio]

- MEMBRANE MODULES
  - Flat sheets
    - Plate and frame — [330-500 m^2/m^3]
    - Spiral wound — [650-800 m^2/m^3]
  - Tubular
    - Tubular (> 5mm)
    - Capillary (0.5-5mm)
    - Hollow fiber (< 0.5mm) — [6500-13000 m^2/m^3]



Membranas artificiales

Inorganic membranes

- ✓ Estabilidad física y química
- ✓ Buena resistencia a la erosión
- ✓ Alto flujo y selectividad

Alto costo de fabricación

Relación area/volume bajo

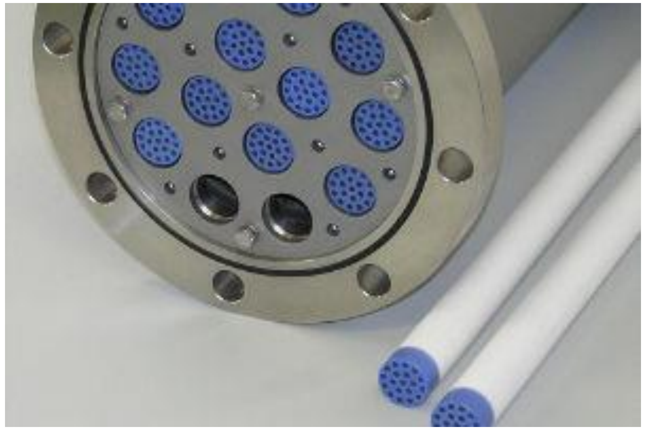
Polymeric membranes

- ✓ Bajo costo

- Resistencia limitada a contaminantes
- Baja estabilidad física y química
- Compensación entre permeabilidad y selectividad

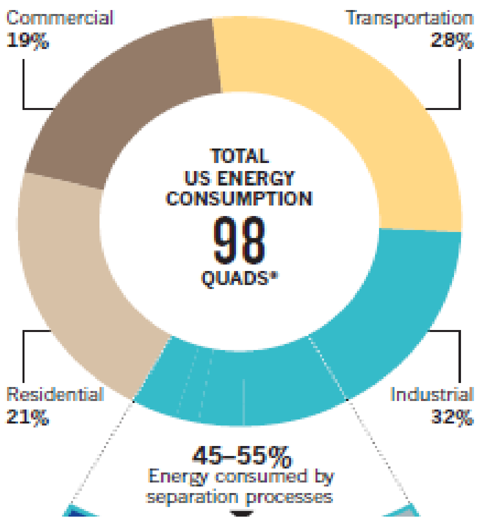
Membranas cerámicas comerciales

Membrane material	Average pore size	Cut-Off
α-Al_2O_3	800nm	
	600nm	
	400nm	600kD
	200nm	400kD
	100nm	300kD
	70nm	200kD
TiO_2	400nm	600kD
	250nm	500kD
	100nm	300kD
ZrO_2	110nm	300kD
γ-Al2O3	10nm	20kD
	5nm	7500D
SiO_2	1,0nm	600D
TiO_2	1,0nm	750D
	0,9nm	450D



7 separaciones para cambiar el mundo

28 APRIL 2016 | VOL 532 | NATURE



Distillation

≈ 8% from total

16 % of total
Separation processes

Thermal separations
- Distillation
- Drying
- Evaporation
- Non-thermal separations

Membrane-based separation would use
90%
less energy than distillation

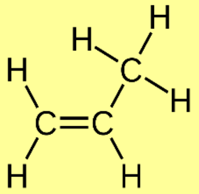
7 separaciones para cambiar el mundo

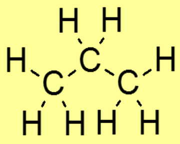
1.- Hidrocarbons del petroleo

✓ El mundo procesa **2 litros de petroleo / persona /dia**, principalmente por destilación

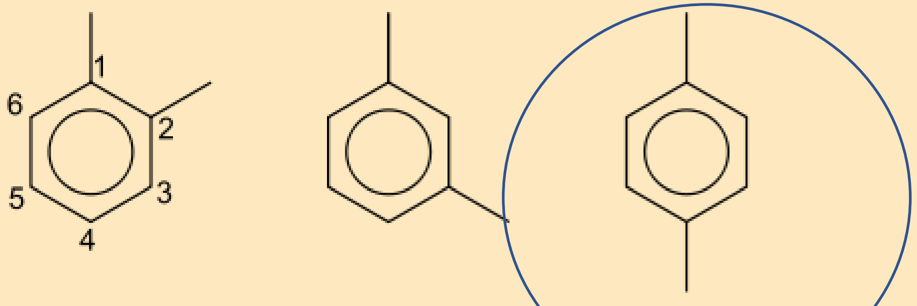
2.- Alkenes from alkanes

✓ Producción global de eteno and propeno ***30 kg/person/year***





3.- Derivados de benzeno



1,2-dimethylbenzene (*ortho*-xylene) 1,3-dimethylbenzene (*meta*-xylene) 1,4-dimethylbenzene (*para*-xylene)

PET polyethylene terephthalate

7 separaciones para cambiar el mundo

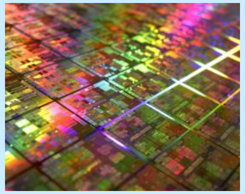
4.- CO_2 de emisiones diluidas (i.e. post-combustion)

400 ppm en el aire

5.- Uranio del agua de mar

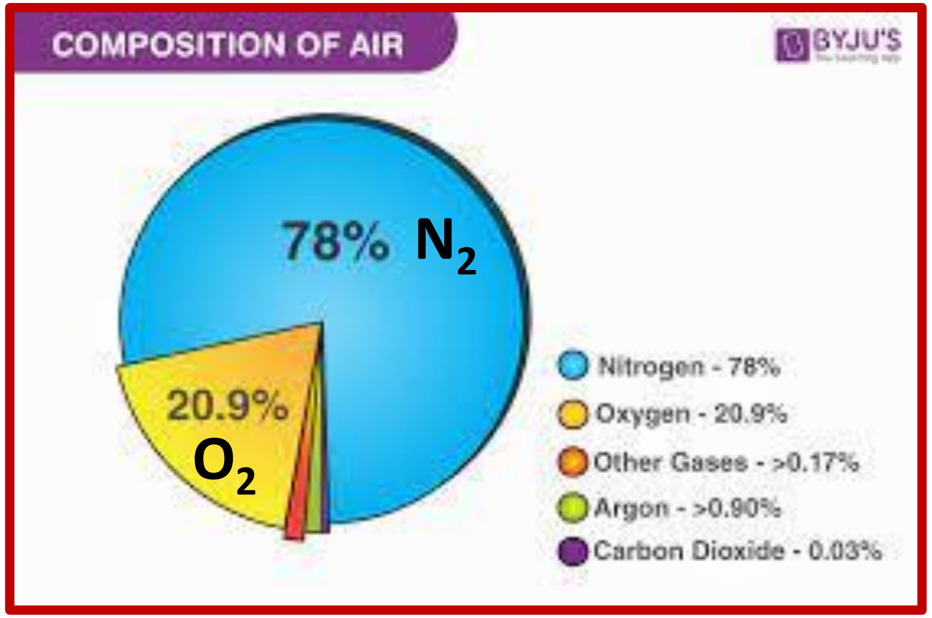
En el agua de mar hay 4 billones de ton de uranio

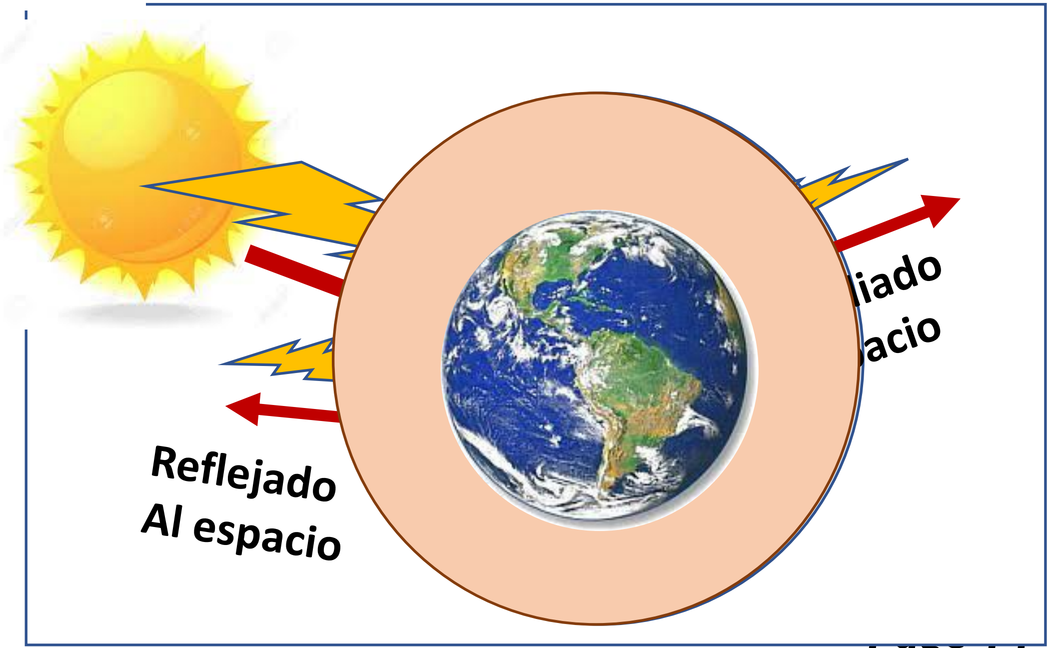
6.- Agua potable del agua de mar

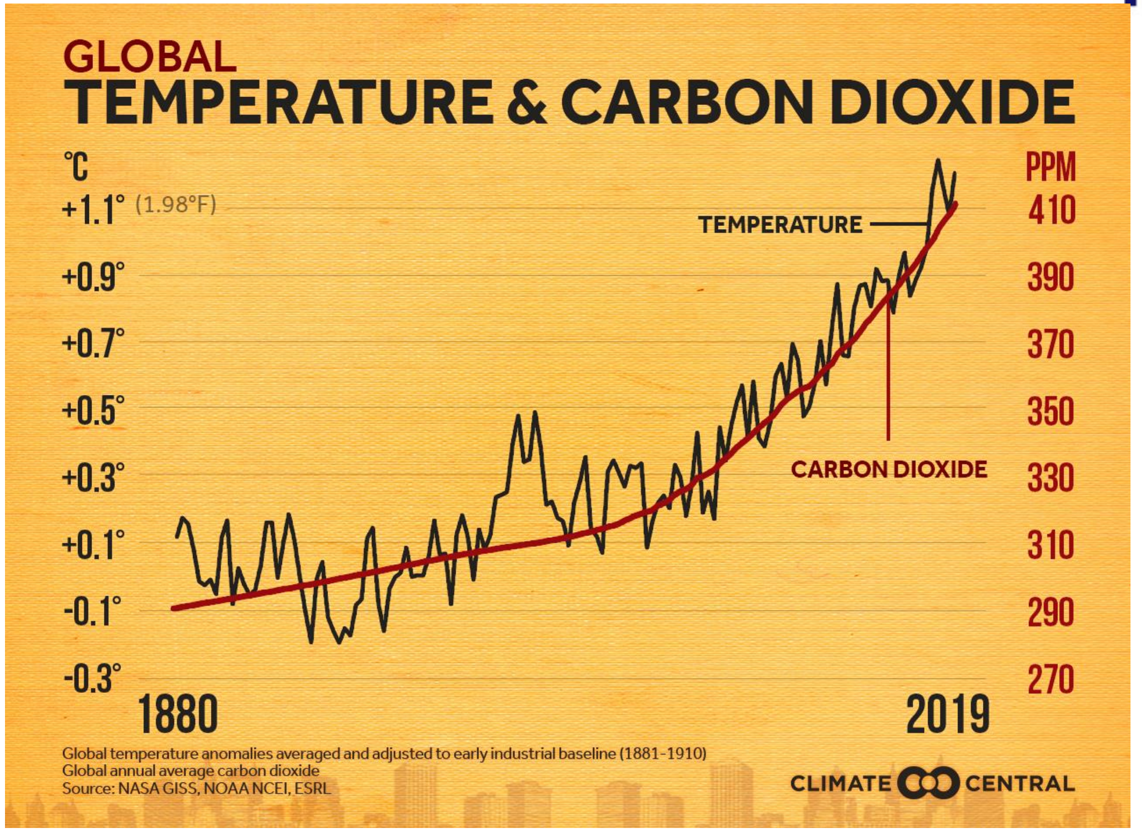


7.- Metales raros

Cambio climático







Combustión

$$CH_4 + O_2 \rightarrow CO_2 + H_2O$$

MacMillan dictionary

Gases efecto invernadero

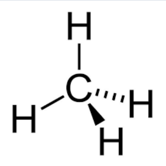
CO_2

80% emisiones

75% combustibles fósiles

Pueden durar miles de años

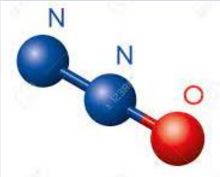
metano



15% emisiones

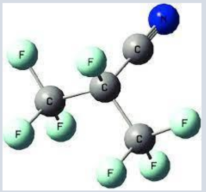
Más potente que CO_2

En atmósfera ~ 10 años



N_2O

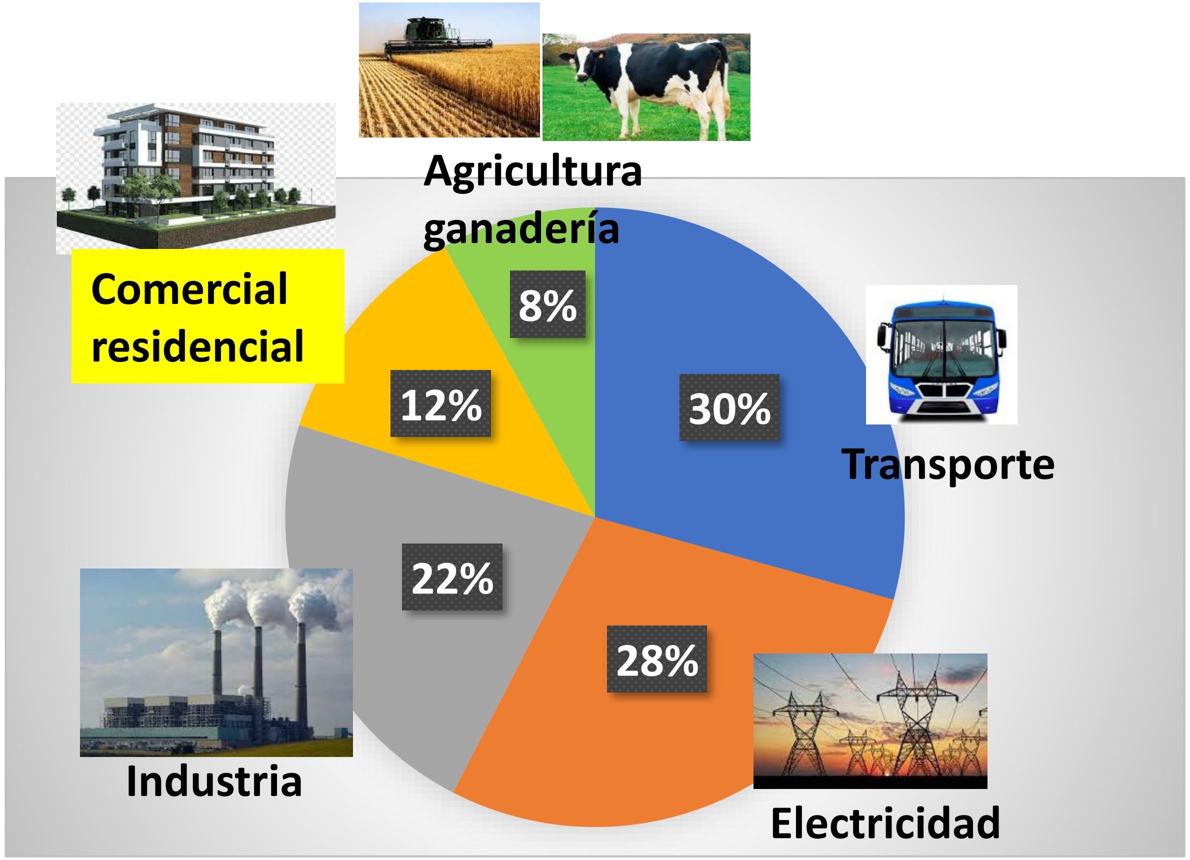
6% emisiones



Gases fluorinados

2% emisiones

Fuentes de gases de efecto invernadero



La union Europea quiere para 2030

- ***cortar un 40%*** la emission de los gases de efecto invernadero
- ***Subir a 32%*** **de energía proveniente** de ***energías renovables.***
- **Aumentar en30 %** la eficiencia energética

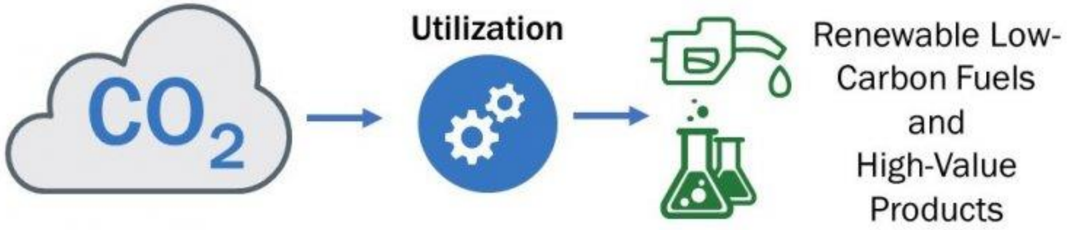
Soluciones para evitar el calentamiento global

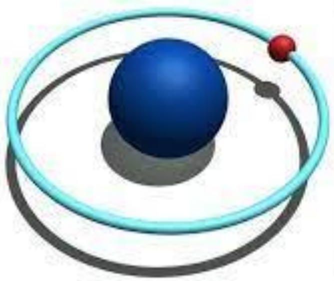
credit : gloly67

- ❑ Reducción del numero de personas en el mundo
- ❑ Reducir emisiones del gases de efecto invernadero
- ❑ Usar combustibles "limpios "

$$H_2 + 0.5\ O_2 \rightarrow H_2O$$

- ❑ Captura y utilización de CO_2





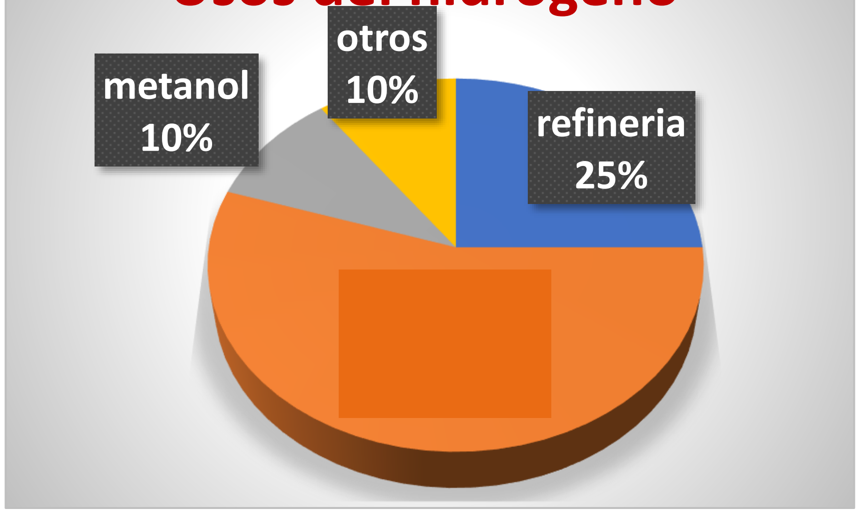
Elemento químico más abundante (75 % de la materia visible del universo).

Cuando se **mezcla con oxígeno** en una variedad de proporciones, de hidrógeno **explota por ignición**

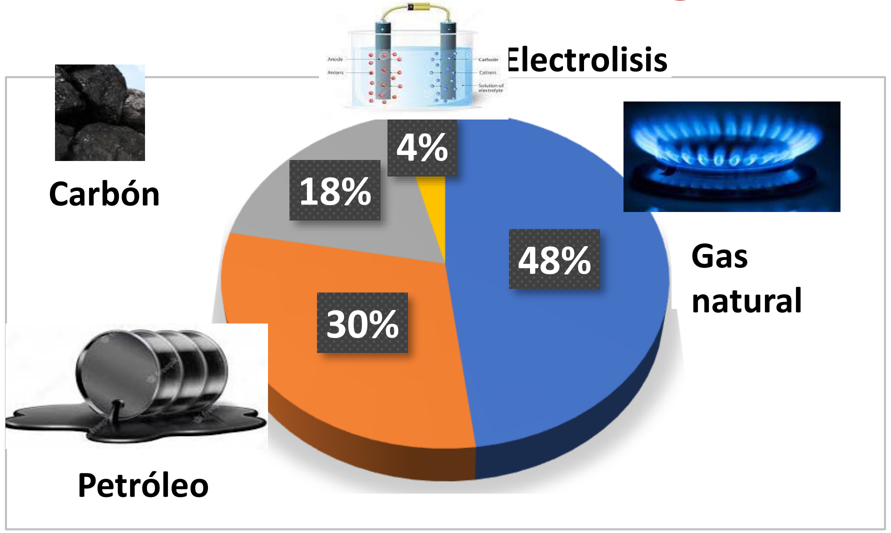
$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l) \quad + \mathbf{572\ \ kJ\ (285.8\ kJ/mol)}$$

No produce gases de efecto invernadero

Usos del hidrógeno

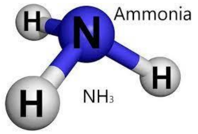


Producción de hidrógeno



85% Fertilizantes

NH_3 , Nitratos



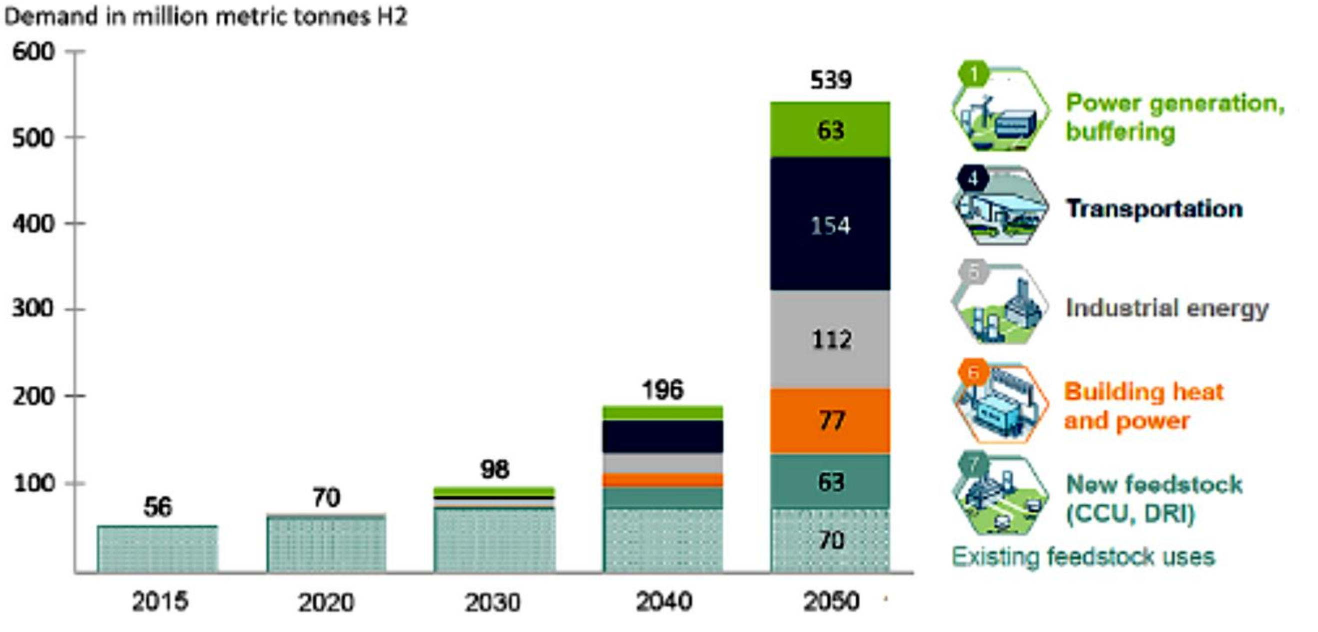
Haber-Bosch (H-B) process (1913)

$6H_2O + 3CH_4 + 4N_2 \rightarrow 3CO_2 + \mathbf{8\ NH_3}$

1.8% energia consumida en el mundo

1.8% CO2 producido en el mundo

Demanda de H_2 aumentará más de 10 veces en 2050



Adapted from *Scaling Up*, Hydrogen Council, 2017. Orginal units in EJ converted to tonnes H2; 1 EJ = 7,000,000 tonnes H2

Celdas de combustible (fuel cells)

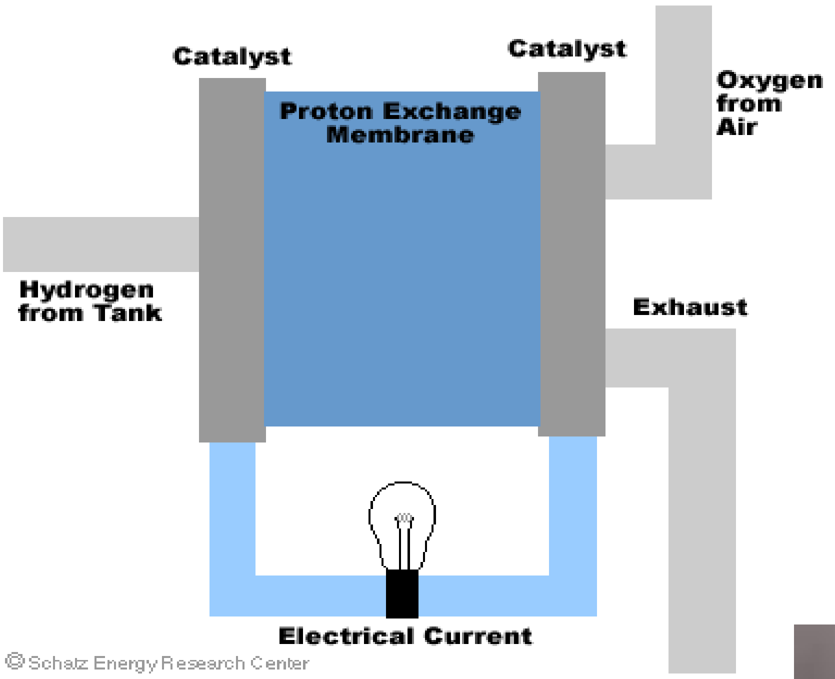
Anode

$2H_2 \rightarrow 4H^+ + 4e^-$

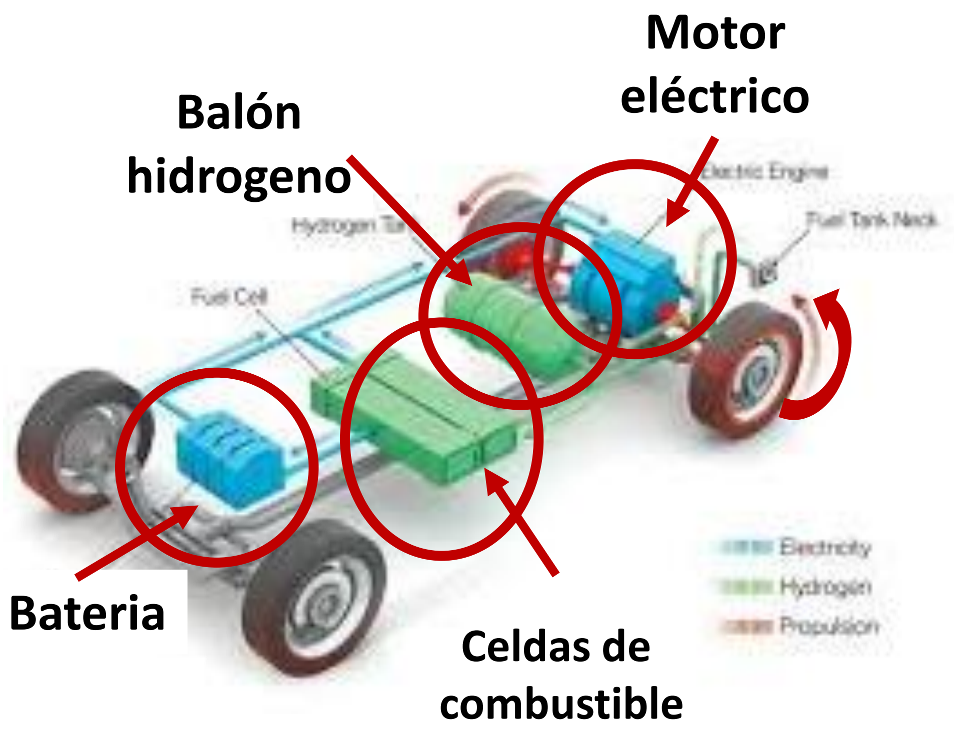
Cátodo

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Overall Cell Reaction: $2H_2 + O_2 \rightarrow 2H_2O$

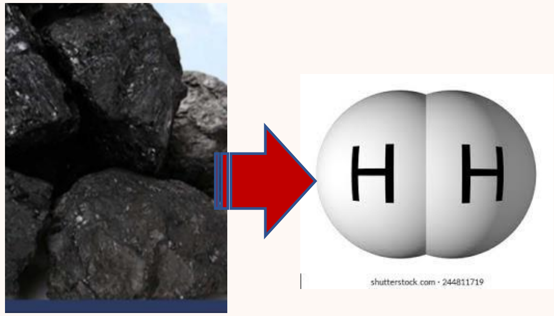


TOYOTA



Hidrógeno café

H_2 producido del carbón



$C + O_2 \rightarrow CO_2$ ***Combustión***

$C + CO_2 \rightarrow 2\,CO$ ***Gasificación***

$2\,CO + 2H_2O \rightarrow 2\,CO_2 + 2H_2$ ***Water gas shift***

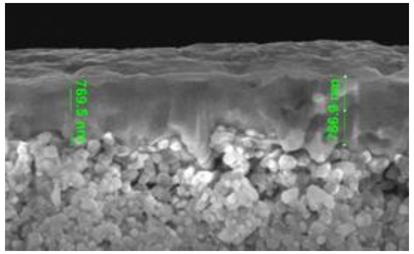
$$2C + O_2 + 2H_2O \rightarrow 2CO_2 + 2H_2$$

Hidrógeno azul

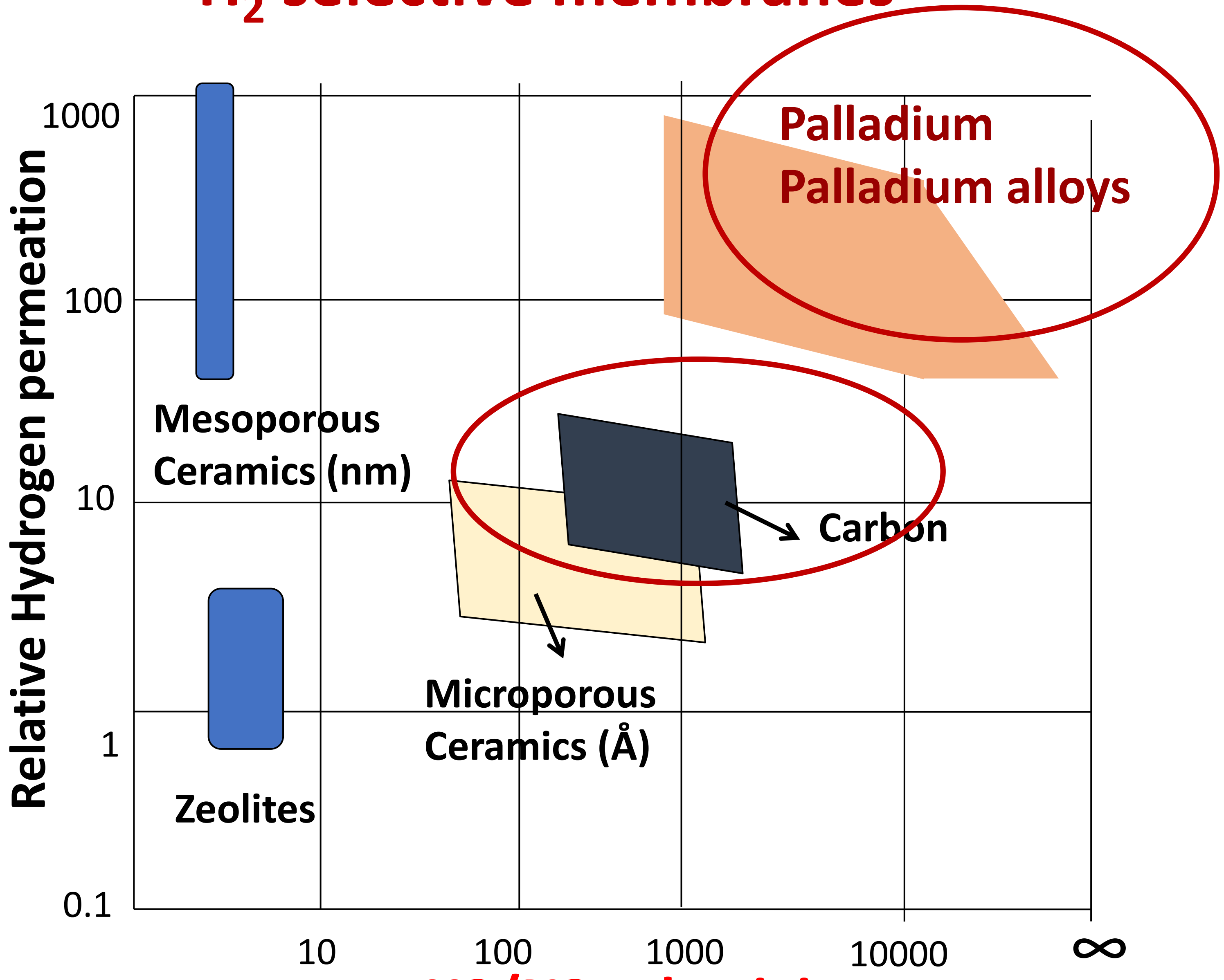
H_2 producido del metano (gas natural) con captura de CO2

Steam reforming of methane (SMR)

$$CH_4 + 2\,H_2O \rightleftarrows CO_2 + 4\,H_2$$



H_2 selective membranes

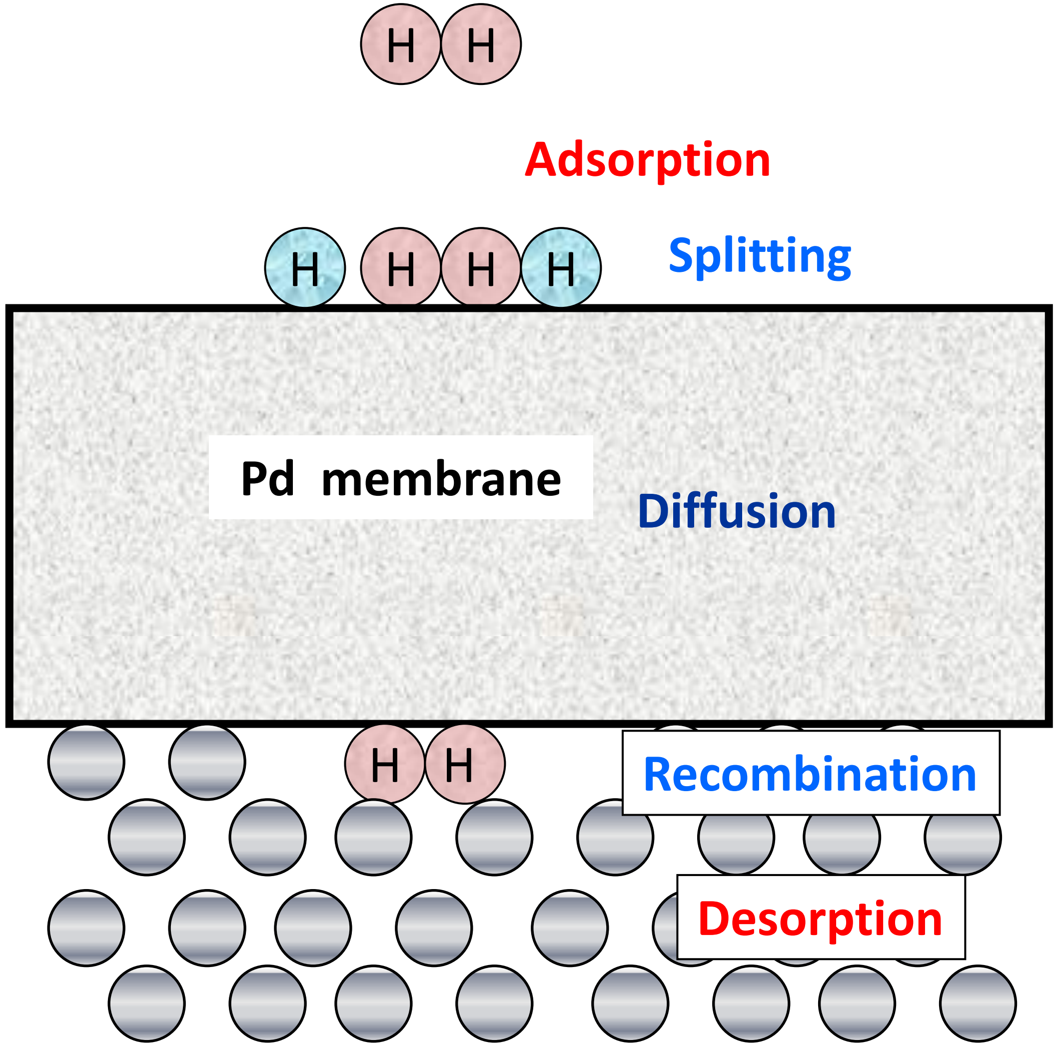


H2 permeation in Pd membranes

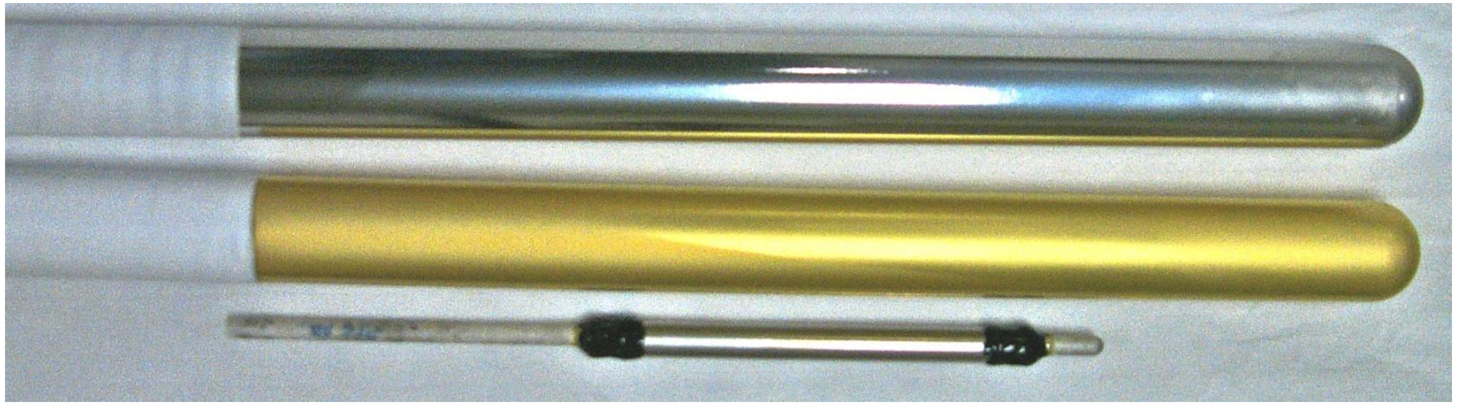
Ultra-thin membranes

-Surface interference
- H_2 splitting

resistance of support



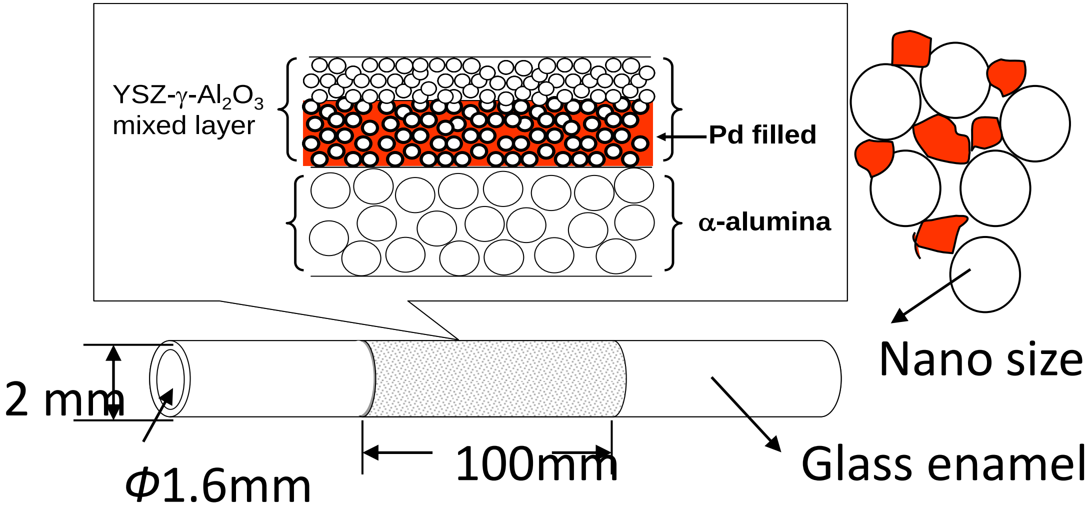
Preparation of Pd-Ag membranes by simultaneous electroless plating deposition



7 Japanese patents

JP2003285451A 2005-03-03
JP4189821 (B2), 2008-12-03
JP4572385 (B2), 2010-11-04
JP4729755 (B2), 2011-07-20
JP4753180 (B2), 2011-08-24
JP 4998881 (B2), 2012-08-15
JP5311536 (B2), 2013-10-09

Pore filled membranes



Pd particles are confined in the nano-space of YSZ-γ-Al_2O_3

SEVENTH FRAMEWORK PROGRAMME
2007- 2013

HORIZON 2020

EU projects on membrane reactors for H_2 production

Water gas shift reaction (WGS)

DEMCAMER Catalytic Membrane Reactors

$$CO + H_2O \rightleftarrows H_2 + CO_2$$

Steam reforming of methane (SMR)

$$CH_4 + 2\,H_2O \rightleftarrows CO_2 + 4\,H_2$$

RE4CELL FERRET BIONICO

Methanol steam reforming

$$CH_3OH + H_2O \rightleftarrows CO_2 + 3\,H_2$$

Ethanol steam reforming

$$C_2H_5\,OH + 3\,H_2O \rightleftarrows 2\,CO_2 + 6\,H_2$$

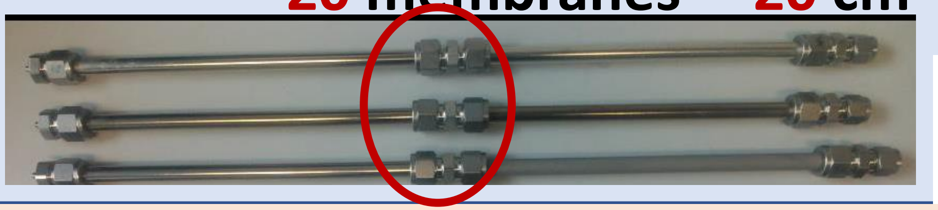
Fluid CELL

Pd membrane reactors at Tecnalia and TU/e

m-CHP

Support Alumina 10/7 mm

20 membranes 20 cm

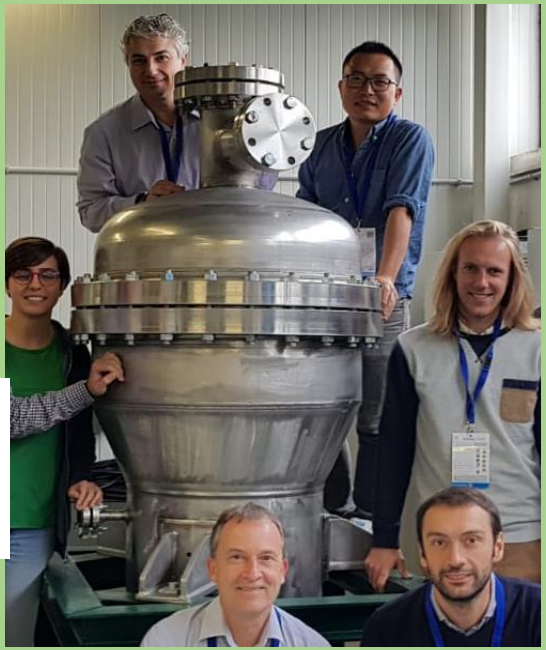


RE4CELL

37 membranes 40 cm

FluidCELL

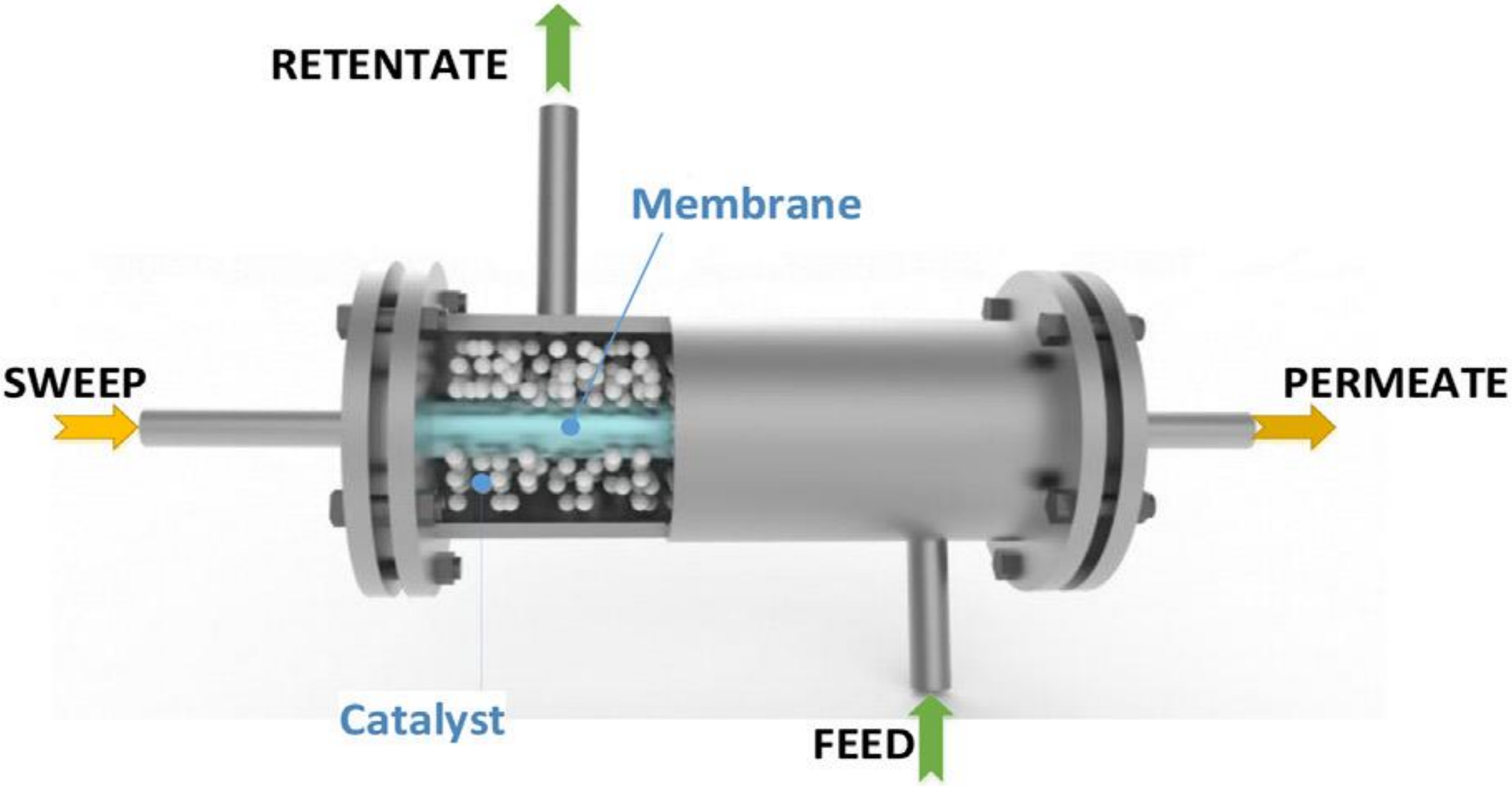
BIONICO



Support Alumina 14/7 mm

125 membranes 45 cm

H_2 production: Conventional Steam Methane Reforming (850 ° C)

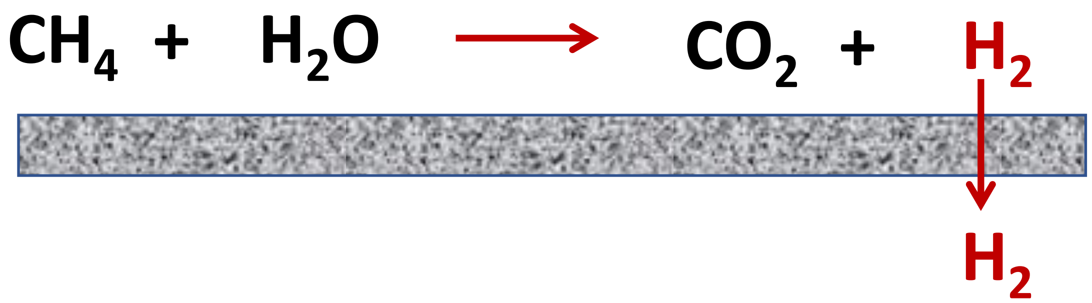


F. Galucci ….. Chemical Engineering Science 92 (2013) 40–66

H_2 production

Steam Methane Reforming / Water Gas Shift

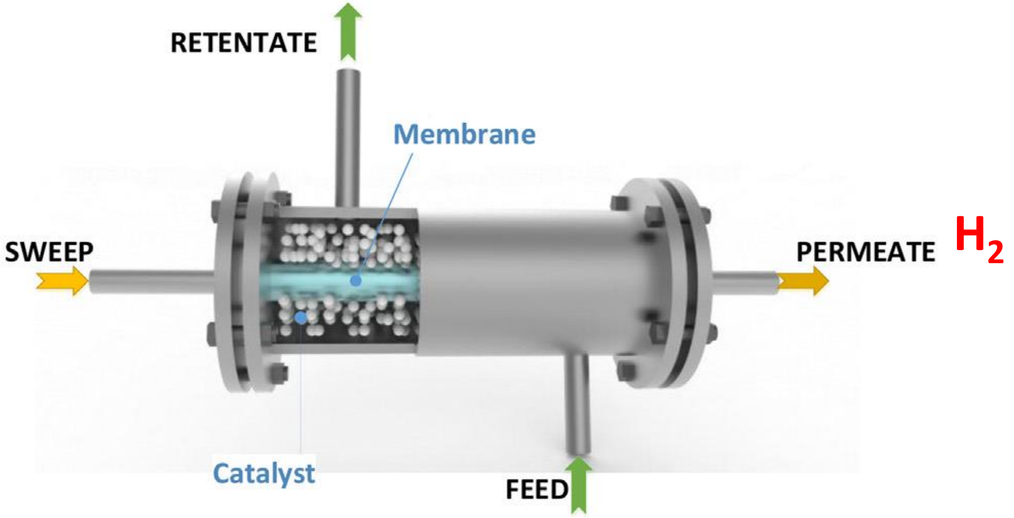
	$\Delta H_{600\,C}$ Kj/mol	Favored Temp	Favored Pressure
Steam Methane Reforming			
$CH_4 + H_2O \rightleftharpoons CO_2 + 3\,H_2$	223.5	High	Low
Water gas shift			
$CO + H_2O \rightleftharpoons CO_2 + H_2$	- 36.1	Low	Independient



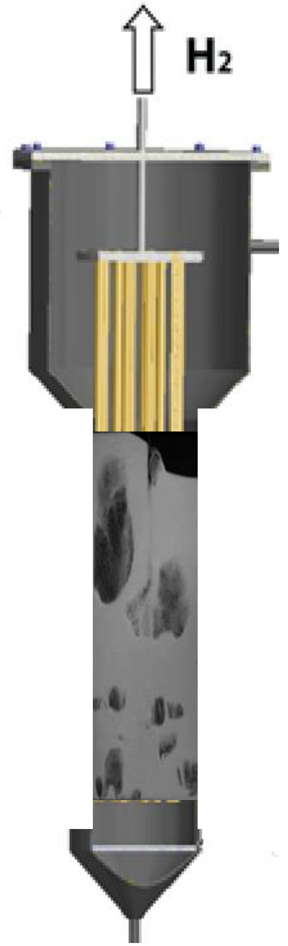
Pd membrane

H_2 production: Membrane reactor

Packed bed

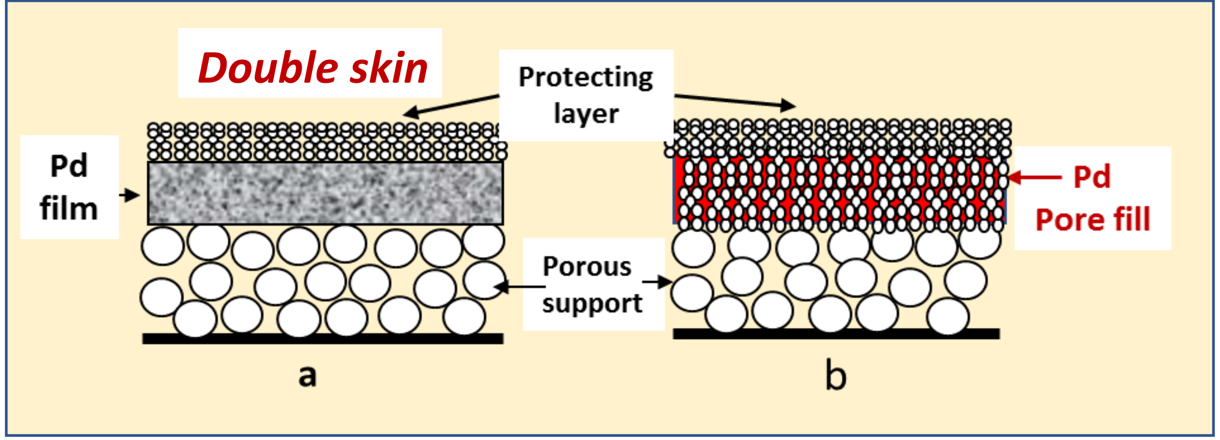


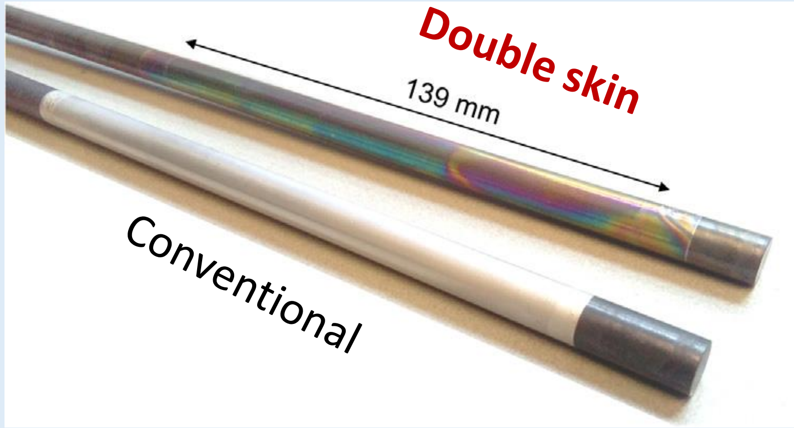
Fluidized bed



- Bed to membrane mass transfer limitations (concentration polarization)
- Pressure drop along the reactor
- Possible intra-particle mass transfer limitation
- Hot spots in highly exothermic reactions

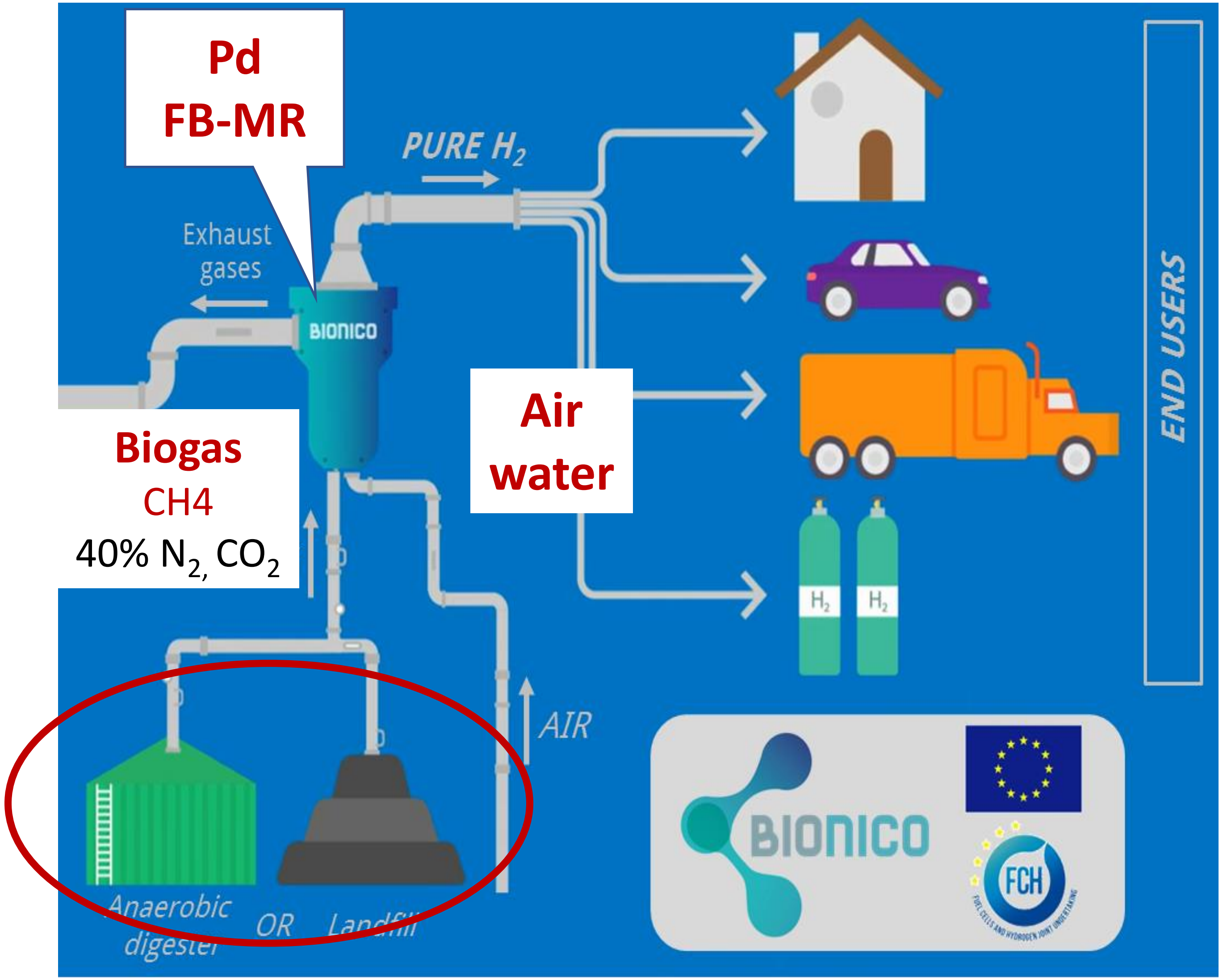
Attrition resistant membranes for fluidized bed Pd MR





Alba Arratibel et.al. J. Membr. Sci. 563 (2018)419

Hidrógeno de biogas



H2 SITE
Membrane reactors for H2 generation

PRODUCCIÓN H2 IN-SITU

Evita los costes de transporte y compresión.

ENGIE

-Generación distribución de electricidad, gas natural, petroleo energías renovables
-La segunda empresa más grande del mundo en servicios públicos

Chilca Central termoeléctrica

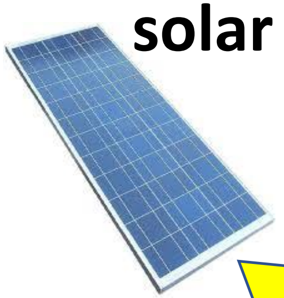
capacidad instalada 114MW

tecnalia TU/e

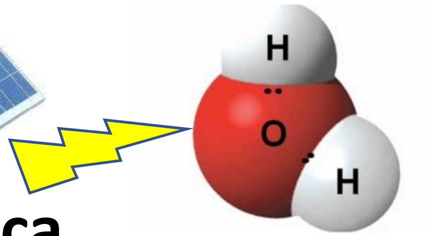
https://www.h2site.eu/es/

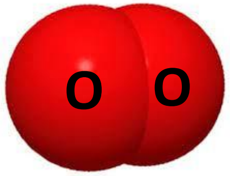
Hidrógeno verde

solar

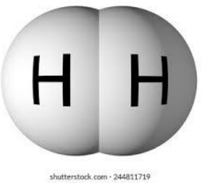


H_2O

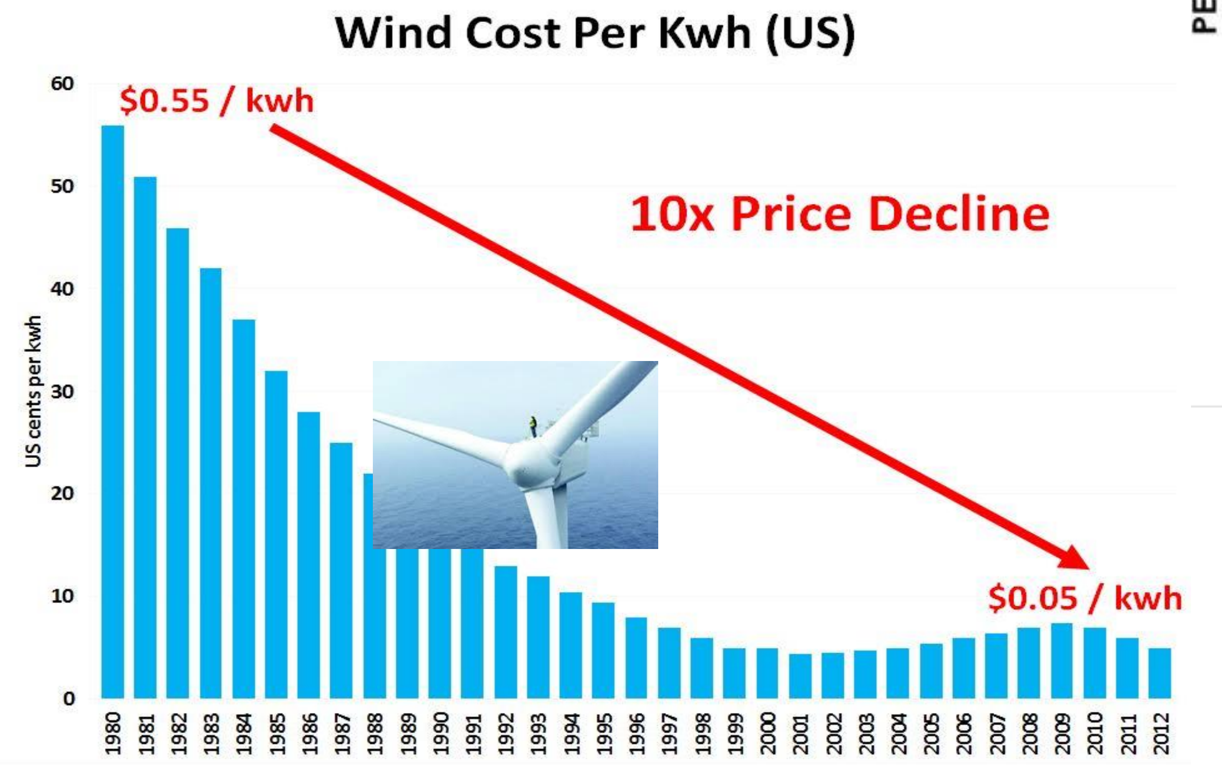


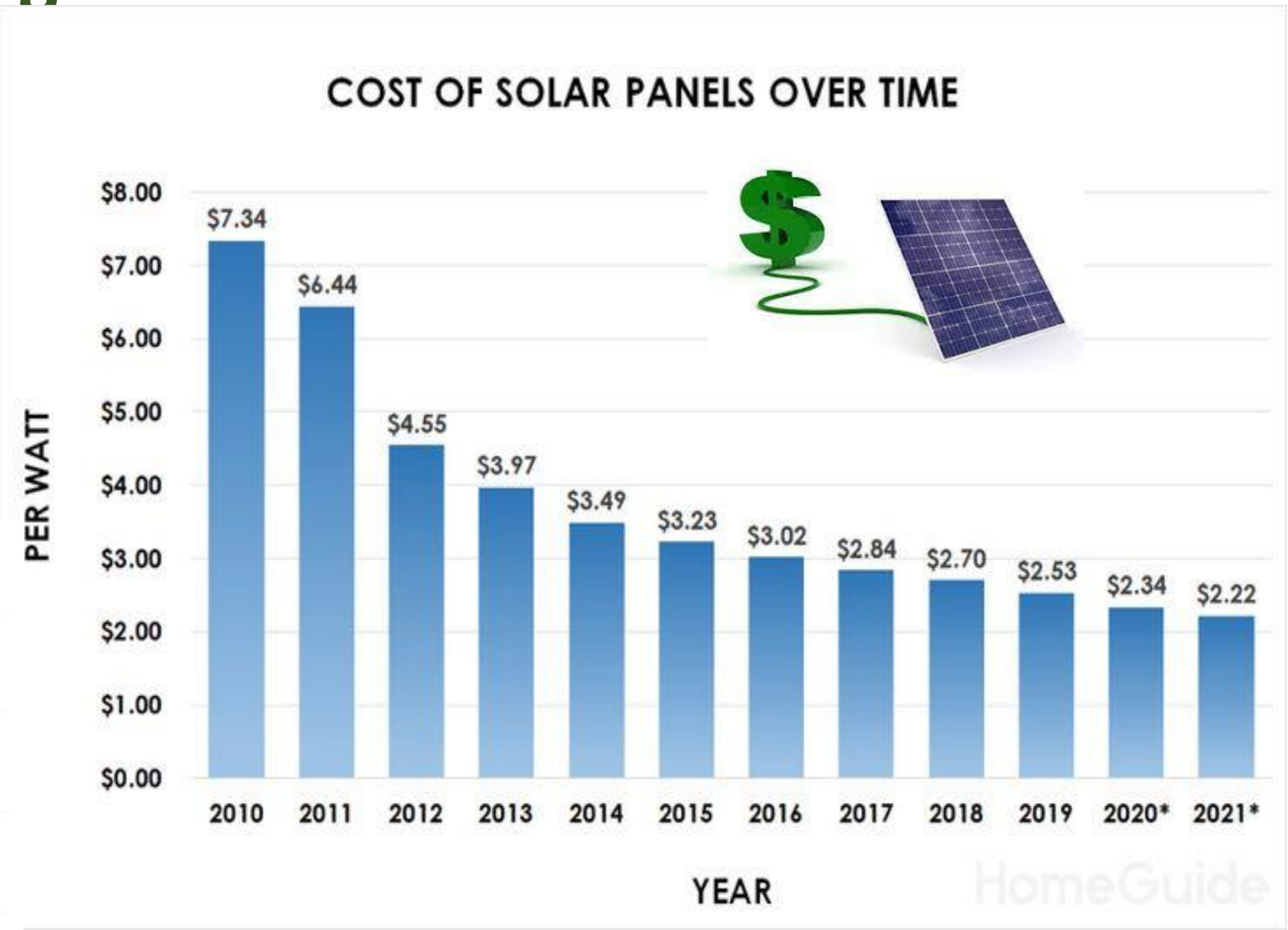


0.5

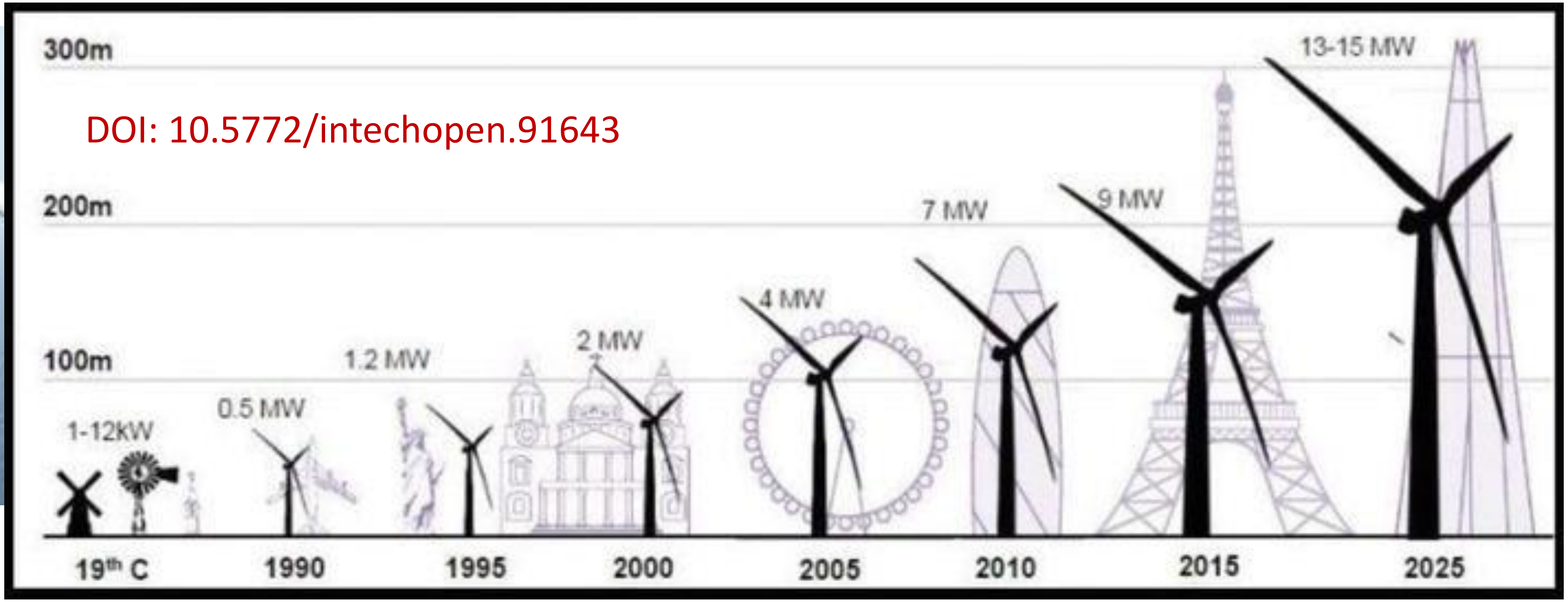


eolica



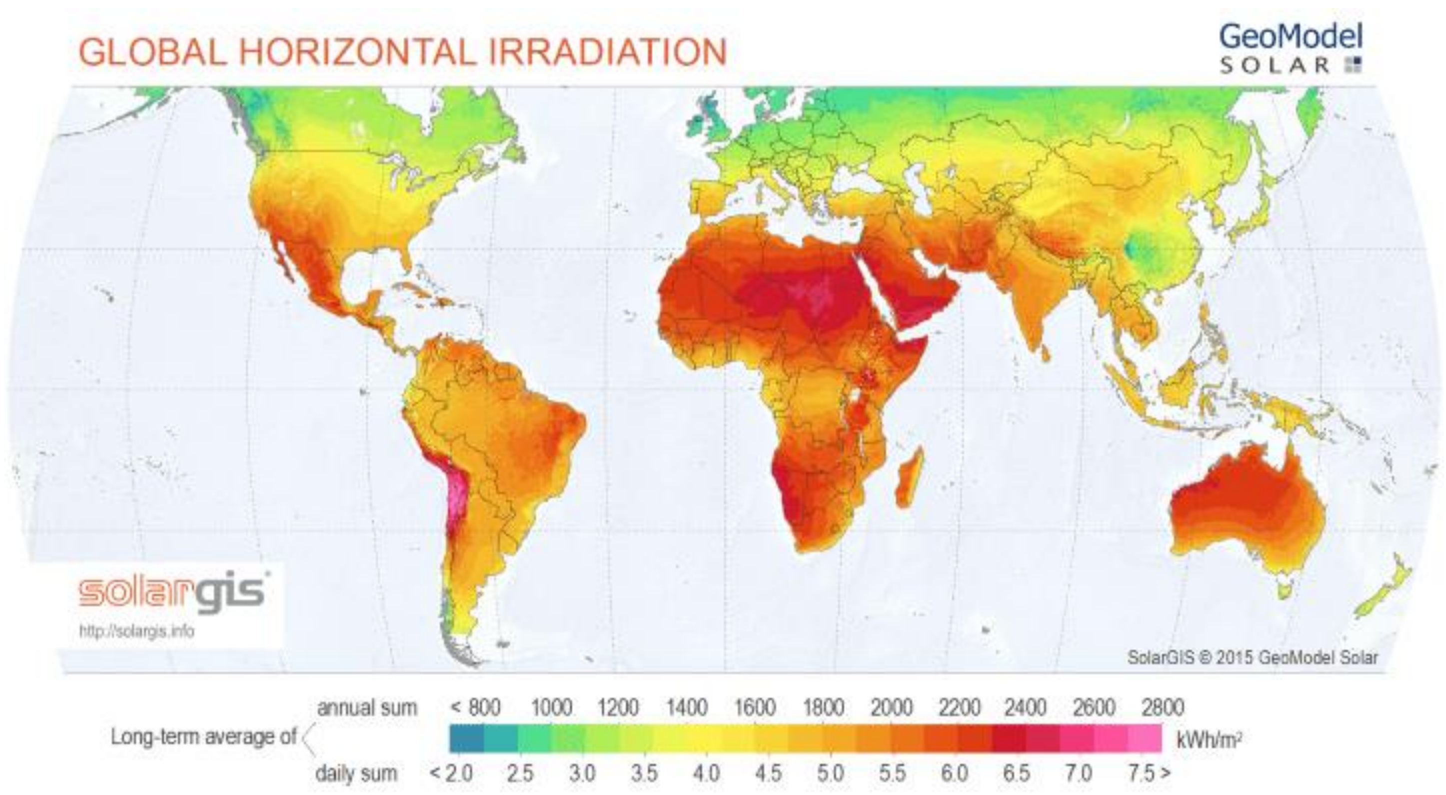


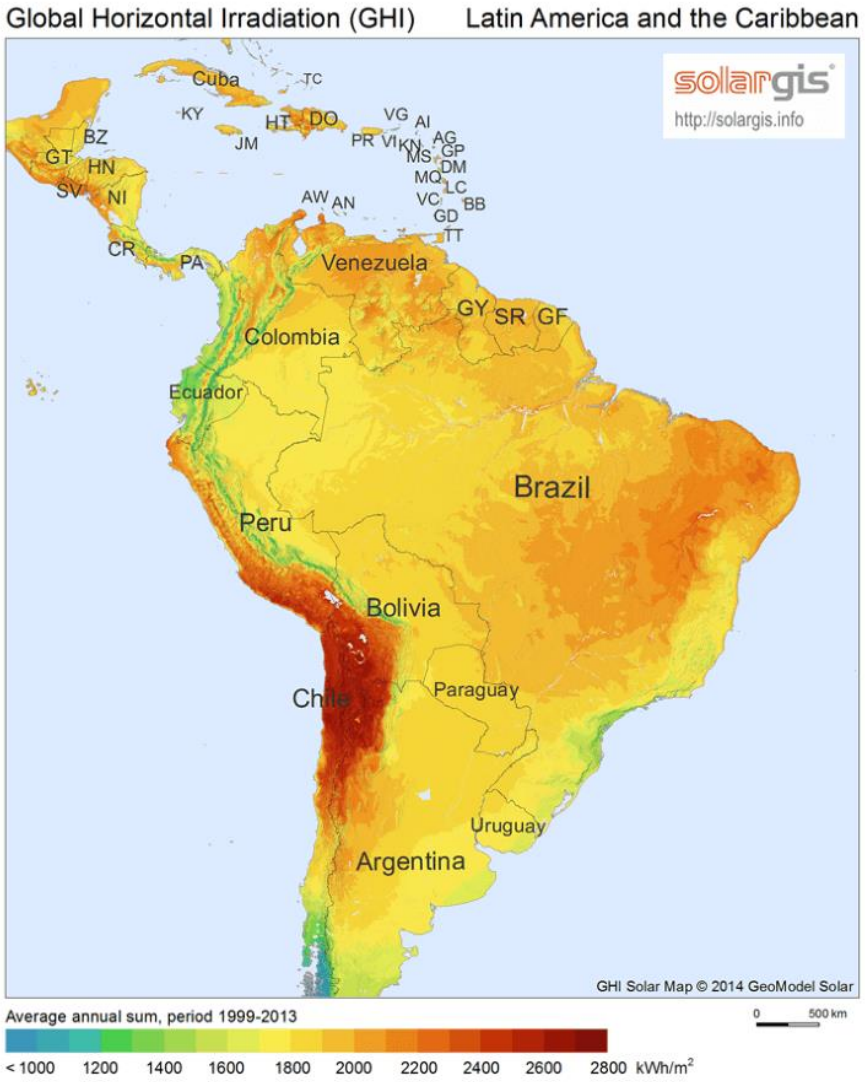
https://homeguide.com/costs/solar-panel-cost



DOI: 10.5772/intechopen.91643

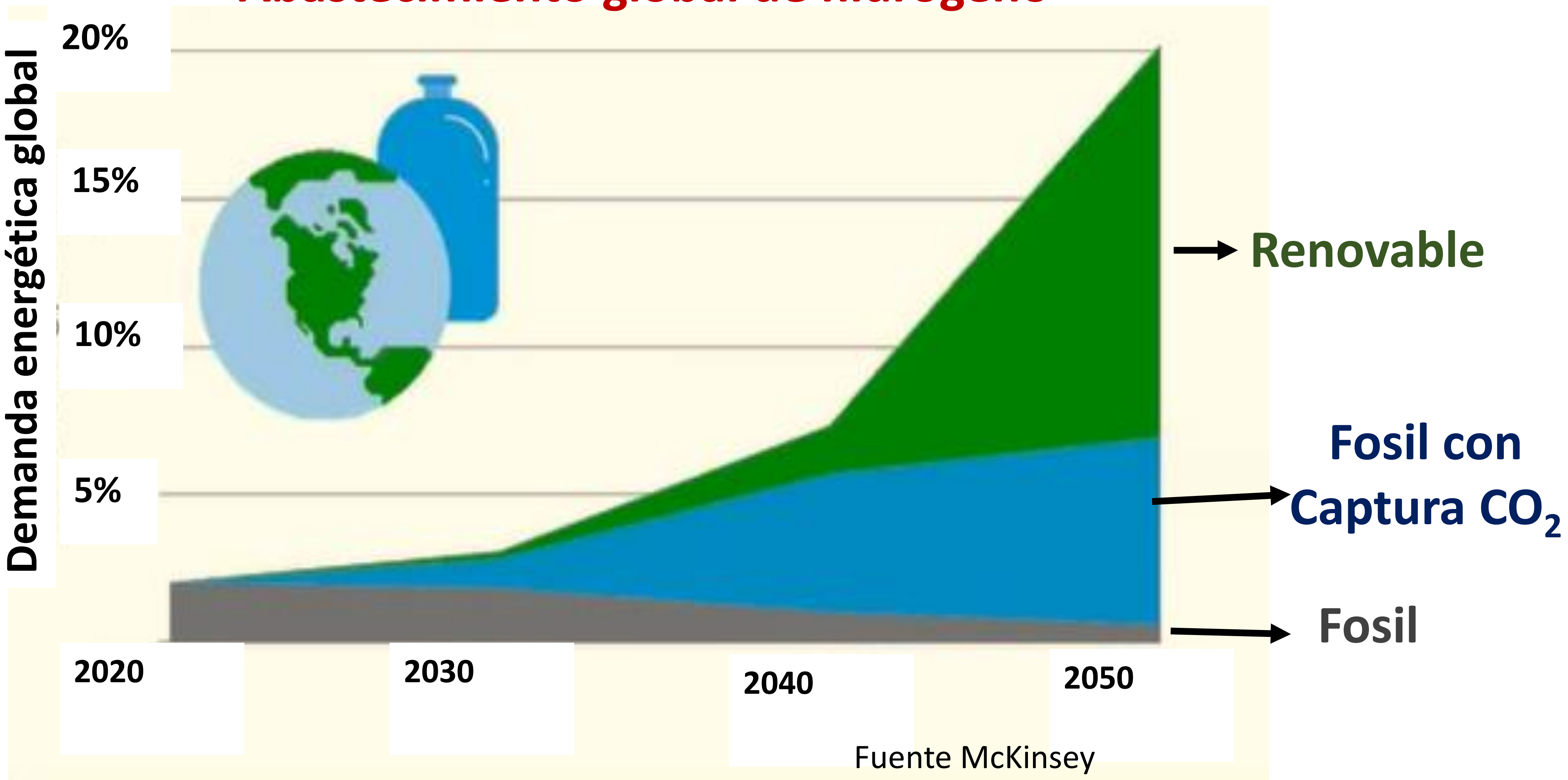
solar energy potential





Energía solar en Chile

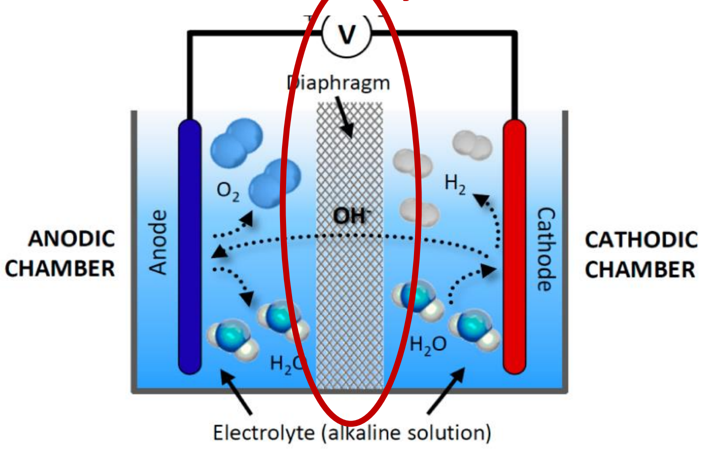
Abastecimiento global de hidrógeno



Fuente McKinsey

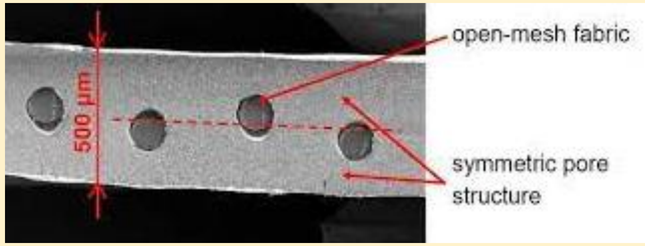
Electrolizadores $H_2O \rightarrow H_2 + 0.5\ O_2$ H_2 verde

Conventional alkaline electrolysis



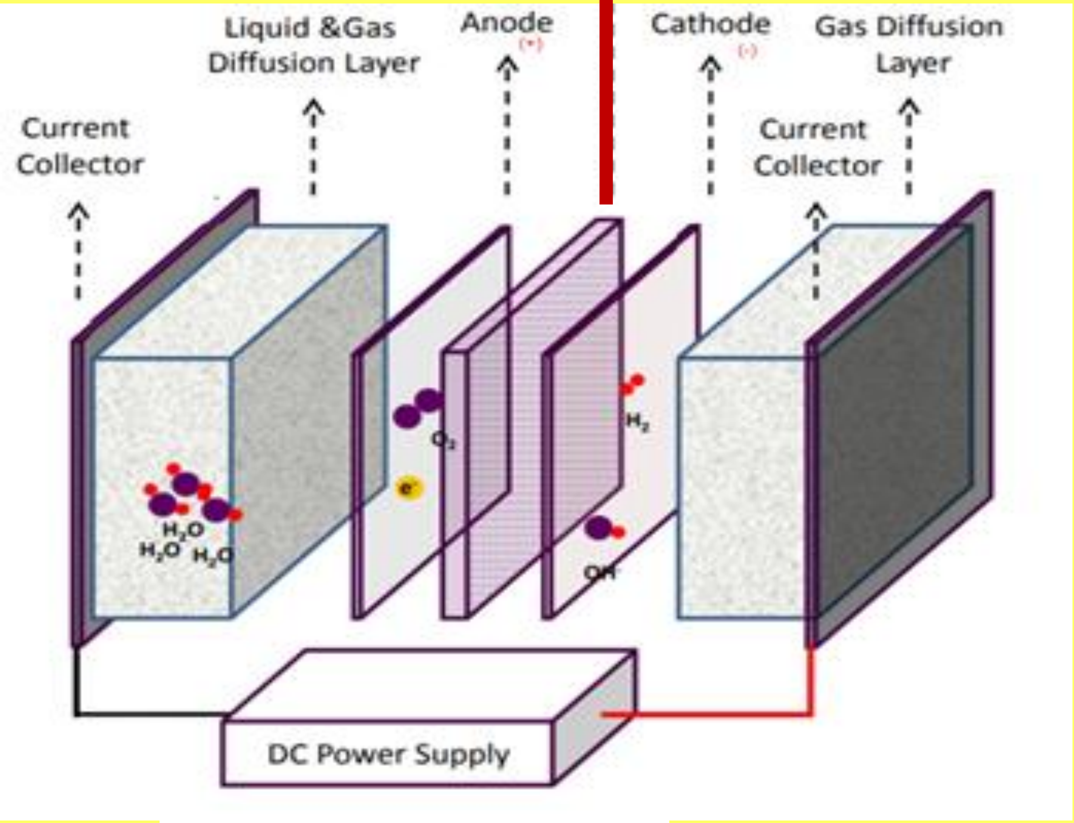
Diaphragm Porous separator Zirfon PERL (500 um thick).

-Hinder gas crossover and limit the mixing of evolved H2 and O2
- Polysulfone filled with ZrO2 nanoparticles (85%)
- Pore average 70- 130 nm



Zero gap (solid) electrolyser

Membrana

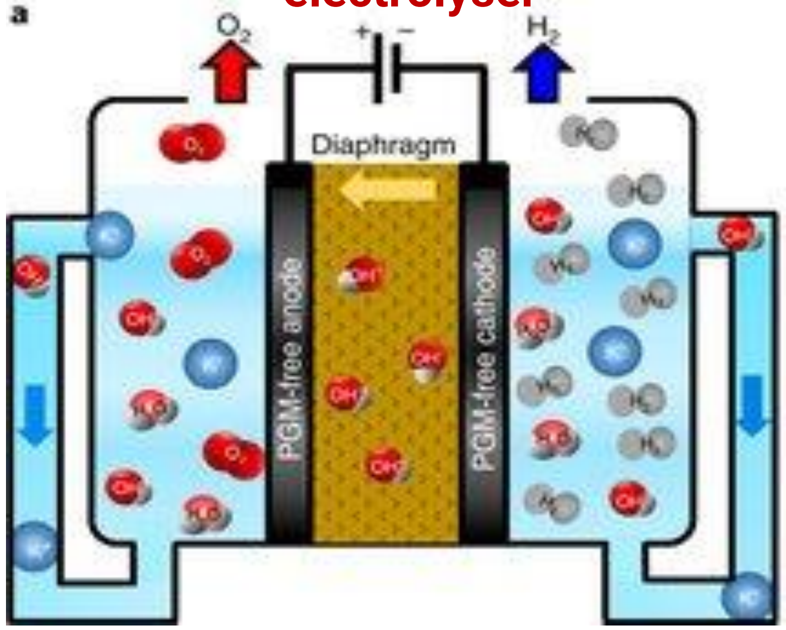


Production H_2 at 30 bar

Celdas de electrolisis de agua de bajas temperatura(zero gap)

$H_2O \rightarrow H_2 + 0.5\ O_2$ H_2 verde

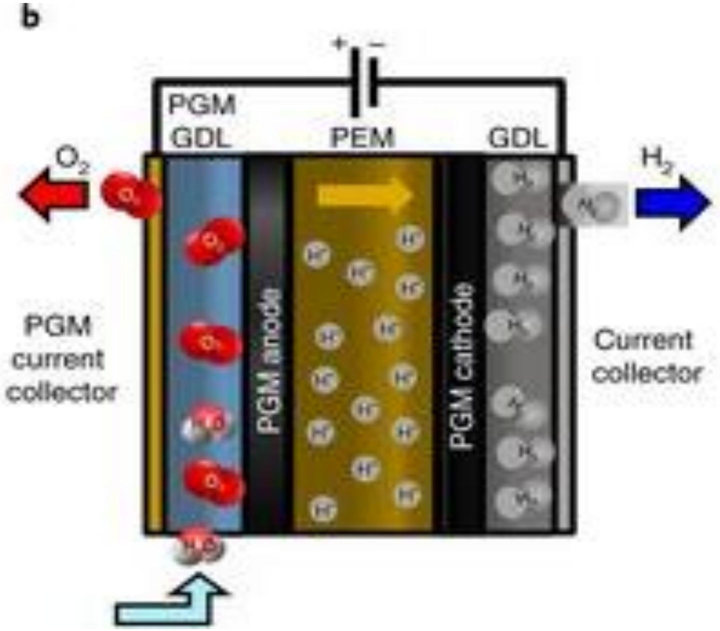
KOH-circulating alkaline electrolyser



PGM-**free** electrode (Ni, Fe)
KOH electrolyte

PGM precious group metals
Pt, Pd, Rh, Ir

PEM electrolyser



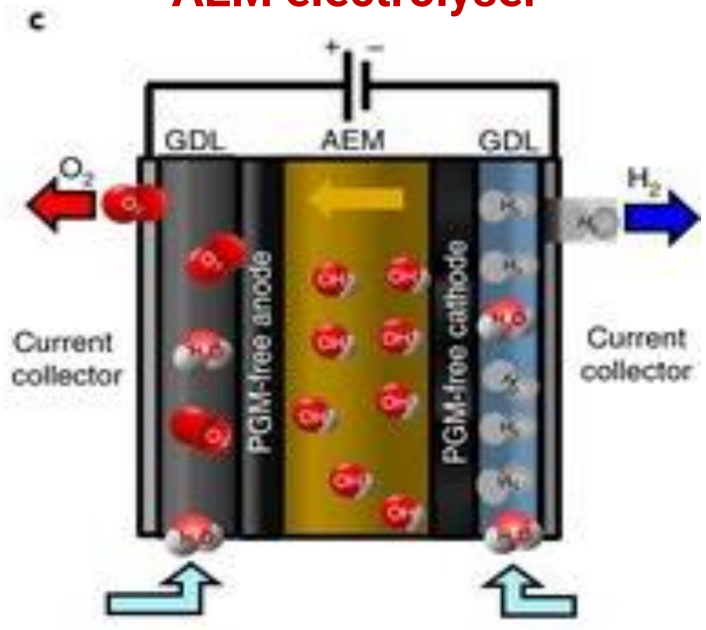
PGM porous electrode (IrO2, Pt),

PEM perfluorosulfonic acid (Nafion)

Ionomer and PGMcurrent collectors..

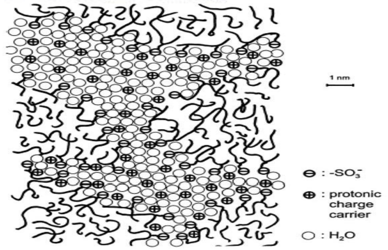
Ti-based current collectors
and separation plates.

AEM electrolyser



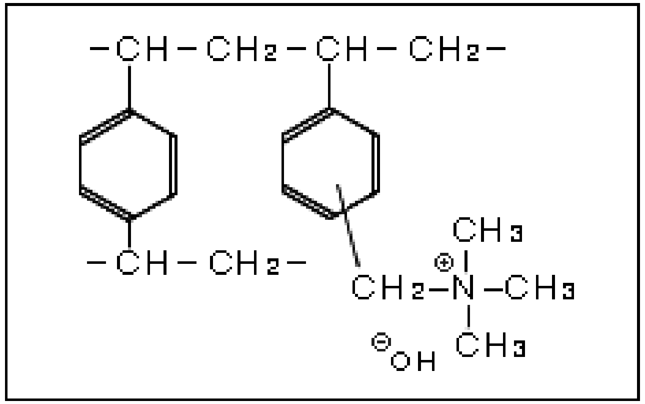
PGM-**free** electrode (Ni based),
AEM/ionomer

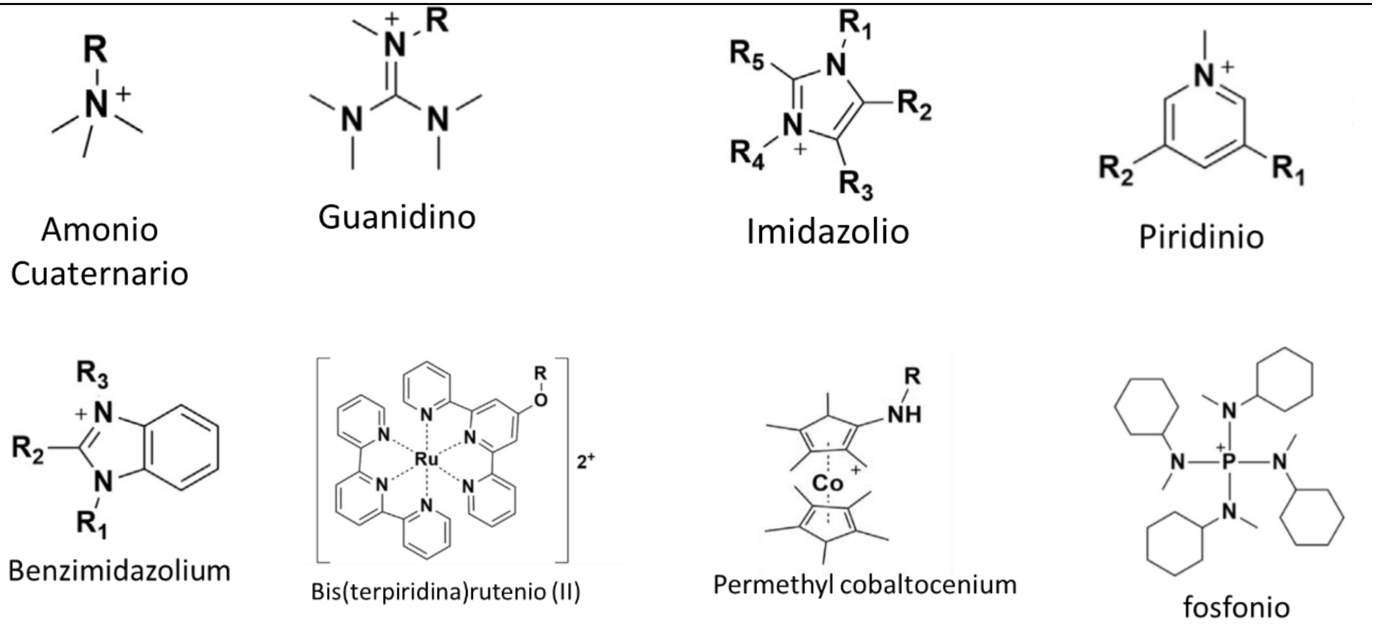
PGM-free current collectors



Membranas de intercambio anionico

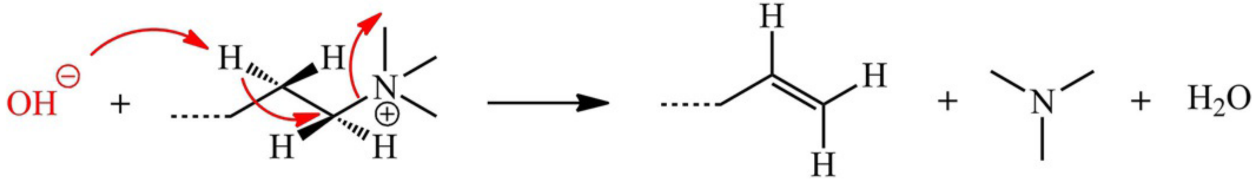
Generally, they are formed by a polymer backbone with anchored cationic groups that confer anion selectivity





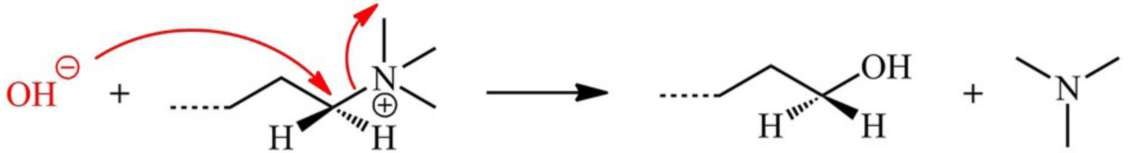
Degradación de la membrana intermcambiadora de aniones

E_2:



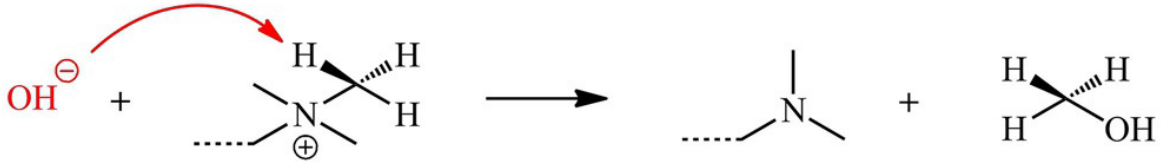
Hofmann elimination (E2)

S_N2:



nucleophilic substitution (SN2)

Y:



ylide formation (Y).

To increase conductivity requires high concentration of OH-

Mobility of OH- is slow requires high concentration of ammonium groups

OH- are less well solvated, and therefore more “naked,” aggressive nucleophiles at low levels of humidification

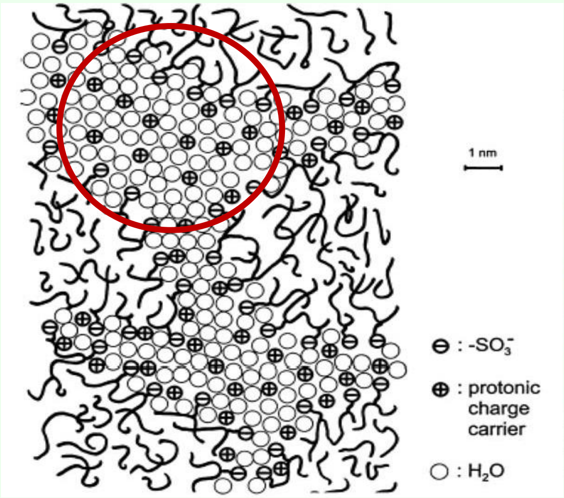
High OH- concentration outside the membrane **affects the osmotic pressure** reducing the water adsorption by the membrane

Problem in membranes for alkaline electrolysers

- **H2 crossover**

High pressure H2

30 bar ΔP



Low solubility of H2 in 30 % KOH

Low H_2 crossover

OH^- low conductivity

High [KOH] 30 %

Highly corrosive

Uso de las lineas de gas para almacenar y distribuir H_2

Blend hydrogen (10 %) with NG

hydrogen membranes

H_2

CH_4

Hybrid system

Membranes

H_2

2- 10 %

Carbon

Palladium

tecnalia Inspiring Business

Electrochemical Hydrogen purification(EHP)

H_2

< 2%

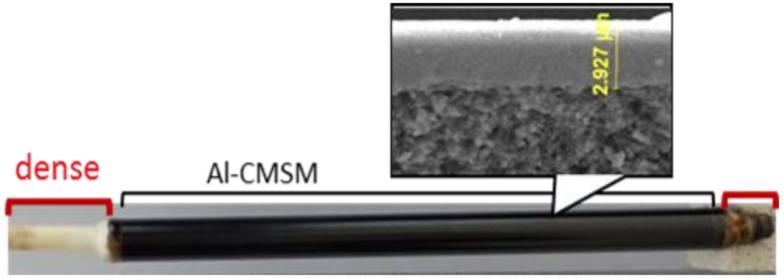
HyET Hydrogen Efficiency Technologies

Temperature Swing Adsoption (TSA)

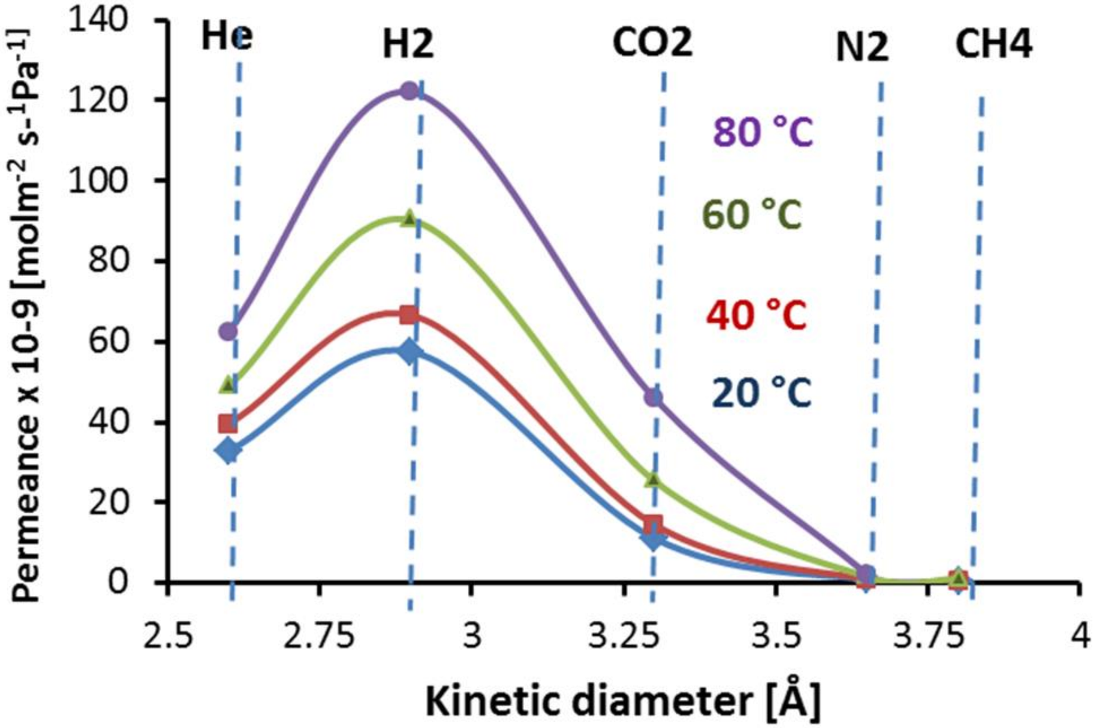
HYGEAR

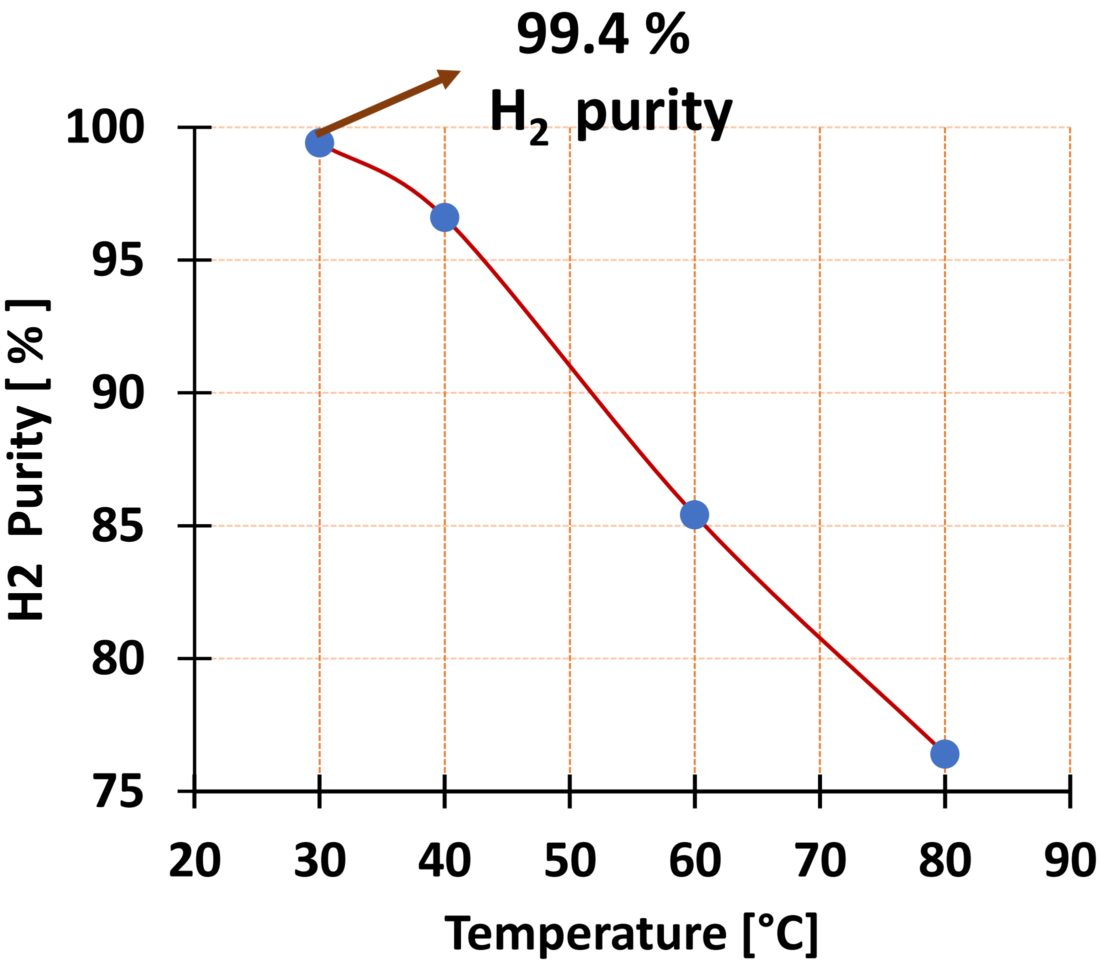
Remove humidity

Membranas de carbono para separación de H2

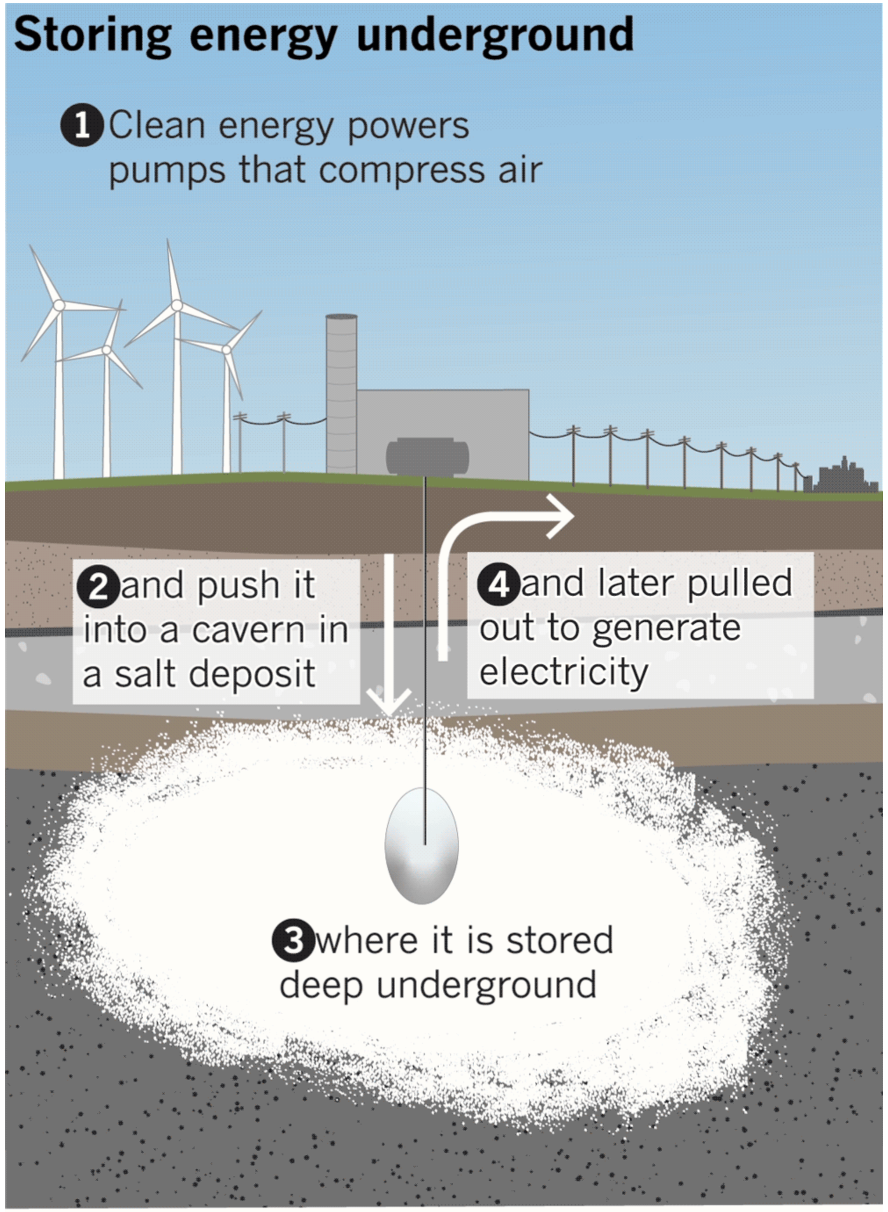


Mix gas 10% H_2 90% CH_4

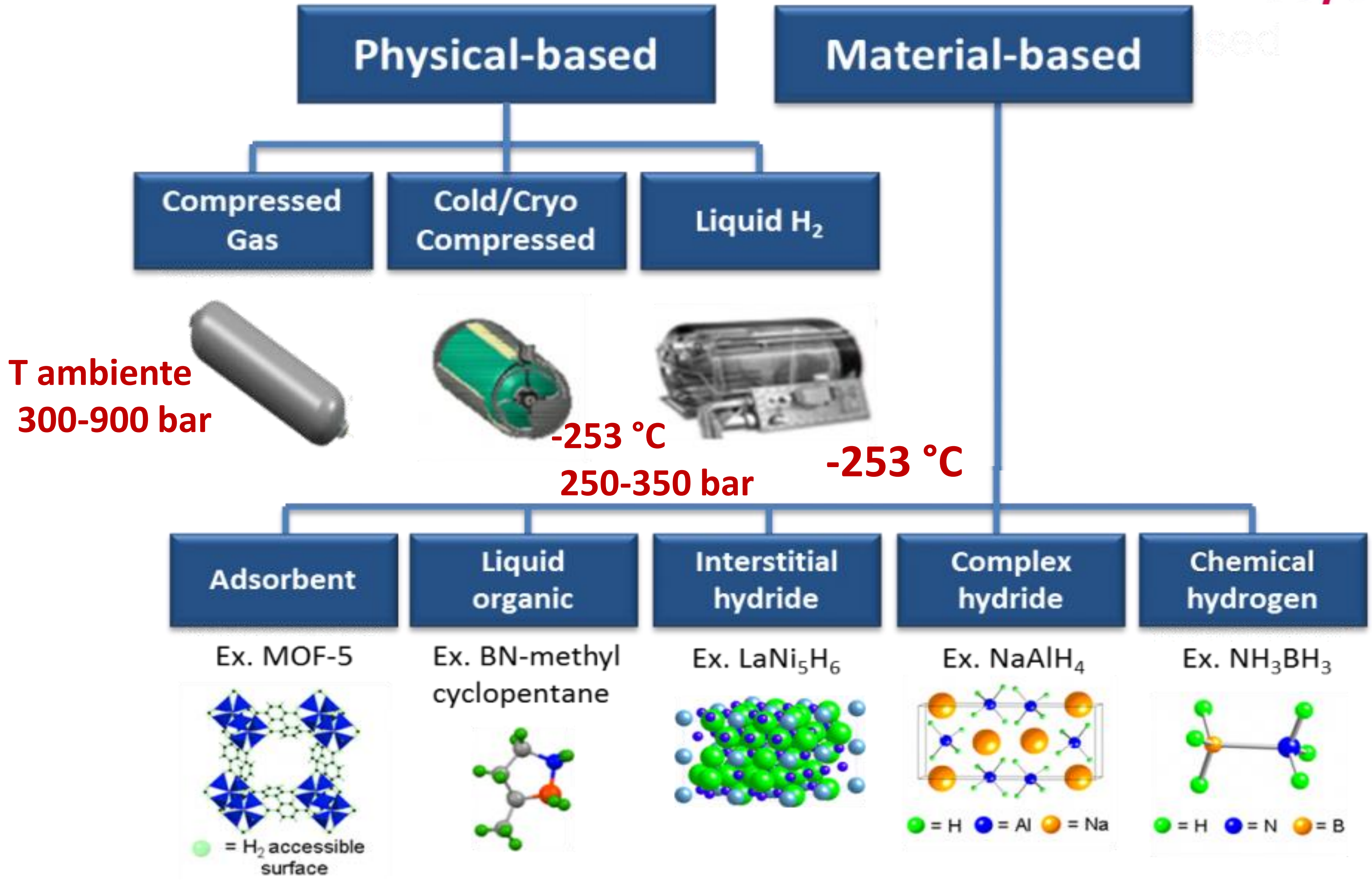




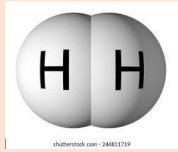
Almacenamiento de hidrógeno en minas de sal



Source: Times Reporting   Jon Schleuss / Los Angeles Times

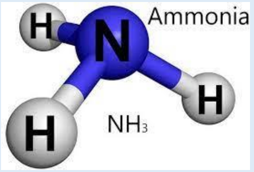

Physical-based
Material-based
Compressed Gas
Cold/Cryo Compressed
Liquid H_2
T ambiente
300-900 bar
-253 °C
250-350 bar
-253 °C
Adsorbent
Liquid organic
Interstitial hydride
Complex hydride
Chemical hydrogen
Ex. MOF-5
= H_2 accessible surface
Ex. BN-methyl cyclopentane
Ex. $LaNi_5H_6$
Ex. $NaAlH_4$
= H = Al = Na
Ex. NH_3BH_3
= H = N = B

H_2



H_2 líquido es al menos 10 veces más caro para producir y ser almacenado que NH_3 porque require alta presión y baja temperatura

NH_3

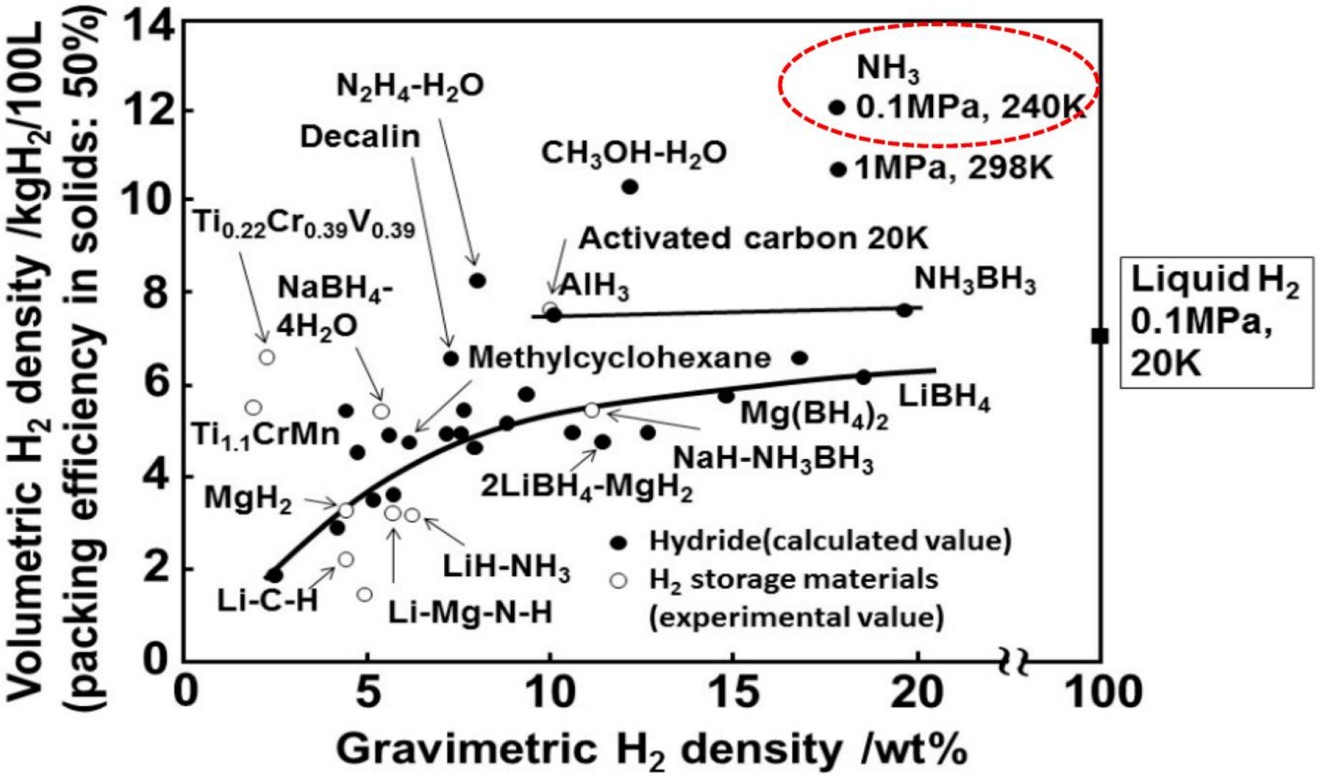


Es líquida a 10 bar o -33 °C

El amoníaco tiene una cadena de suministro y almacenamiento bien establecida

NH_3 se usó en máquinas de combustion interna desde 1800

The density of hydrogen in hydrogen carriers



Energies **2021**, *14*(13), 3732

$$2\ NH_3 \rightarrow 3H_2 + N_2$$

areNH₃a

Ammonia to Hydrogen Project Backed by Government

(https://www.twinfm.com/) / Content (https://www.twinfm.com/content) / Energy Management (/content/energy-management) / Ammonia to Hydrogen Project Backed by Government

01 June 2022 | Updated 08 June 2022

Tyseley Energy Park is to host a world-leading ammonia to hydrogen project with new government backing.

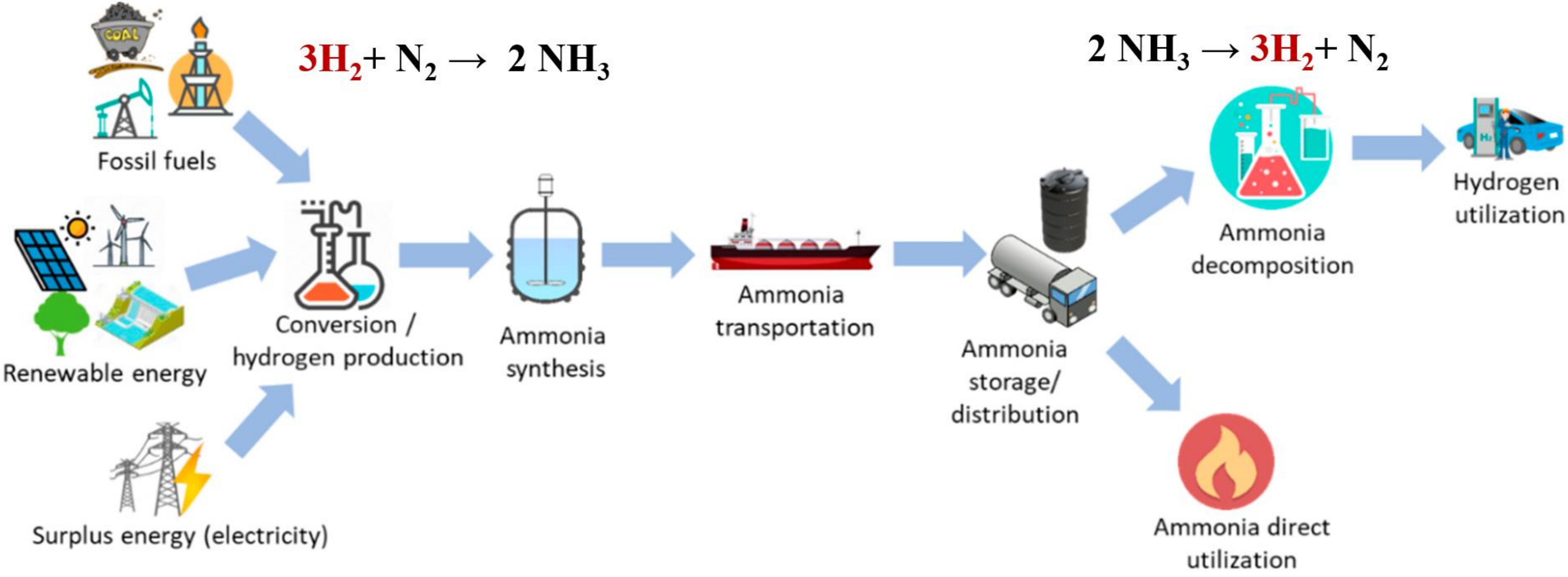
$$2\ NH_3 \rightarrow 3H_2 + N_2$$

The demonstration unit is based on innovative technology developed by H2SITE and is located at Tyseley Energy Park, a strategic energy and resource hub in the West Midlands.

Rutas de producción y utilización de ammonia en el sector anergia

$3H_2 + N_2 \rightarrow 2\,NH_3$

$2\,NH_3 \rightarrow 3H_2 + N_2$

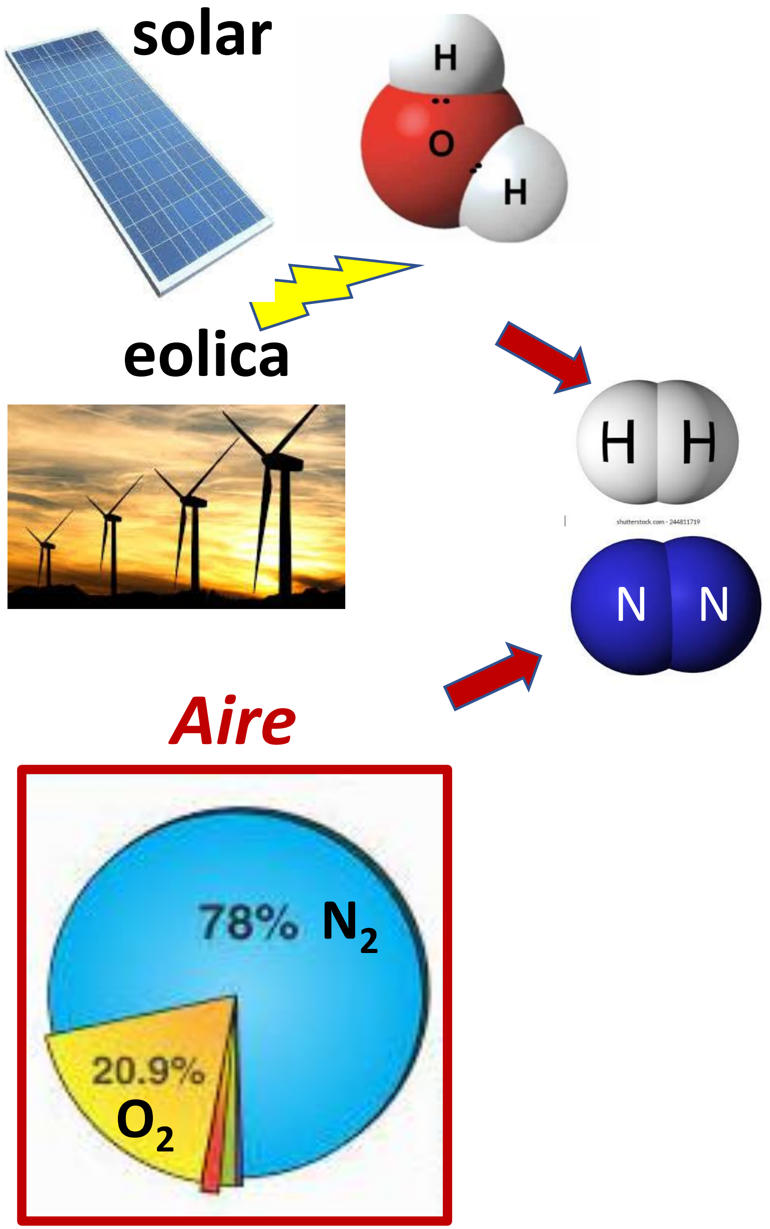


https://doi.org/10.3390/en13123062

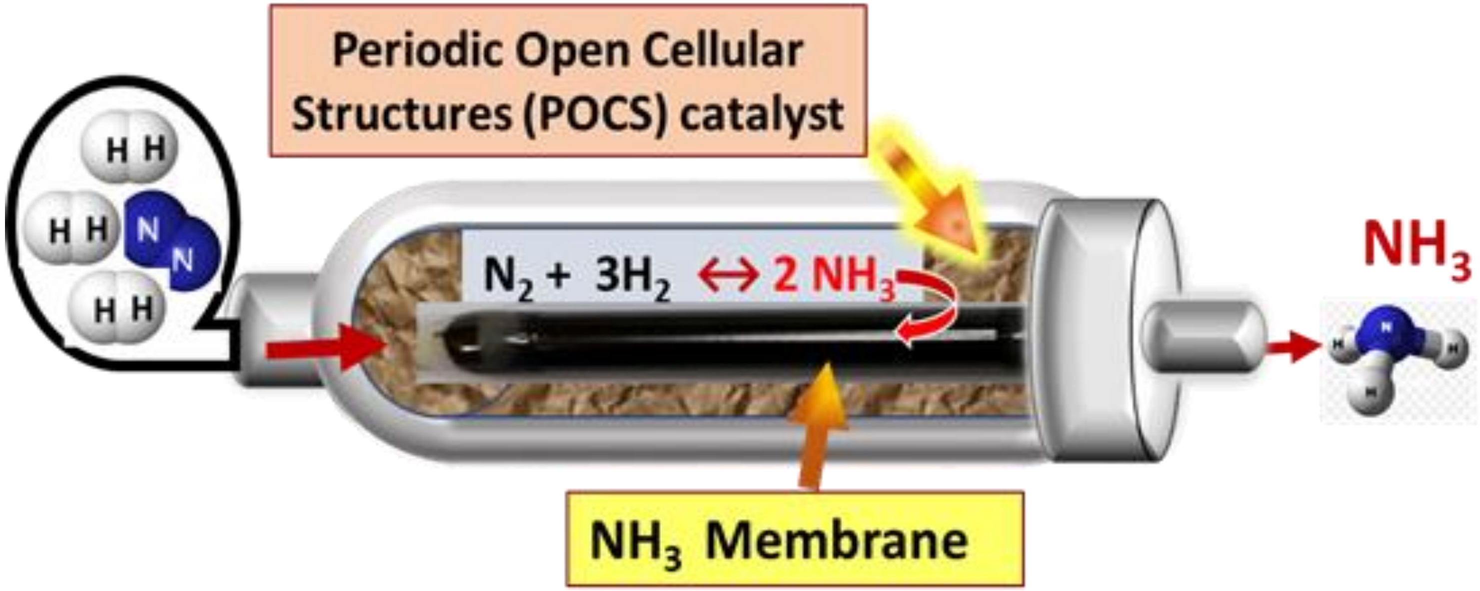
Síntesis de amonia

Haber-Bosch (H-B) process (1913)

$$6H_2O + 3CH_4 + 4N_2 \rightarrow 3CO_2 + \mathbf{8\ NH_3}$$



CATALYTIC MEMBRANE REACTOR (CMR)



Síntesis de ammonia usando Reactores de membrana

AMBHER Julio 2022 - 4 años

Participant legal name	Short name	Type	Country
FUNDACION TECNALIA RESEARCH & INNOVATION	TEC	RTO	ES
TECHNISCHE UNIVERSITEIT EINDHOVEN	TUE	UNI	NL
CONSIGLIO NAZIONALE DELLE RICERCHE	CNR	RTO	IT
THE UNIVERSITY OF BIRMINGHAM	UoB	UNI	UK
UNIVERSITEIT UTRECHT	UU	UNI	NL
AGENCIA ESTATAL CONSEJO SUPERIOR DE	CSIC	RTO	ES
MAX PLANCK INSTITUT FUER	MPI	RTO	DE
UNITED KINGDOM RESEARCH AND INNOVATION	UKRI	RTO	UK
1Cube B.V.	1CUBE	SME	NL
RINA CONSULTING SPA	RINA-C	LE	IT
CENTRE NATIONAL DE LA RECHERCHE	CNRS	RTO	FR
THYSSENKRUPP INDUSTRIAL SOLUTIONS AG	TK	LE	DE
JOHNSON MATTHEY PLC	JM	LE	UK
IBERDROLA CLIENTES SOCIEDAD ANONIMA	IBER	LE	ES
MAHYTEC SARL	MAH	SME	FR
ENGIE	ENGIE	LE	FR
*BELGISCH LABORATORIUM VAN DE ELEKTRICITEITSINDUSTRIE LABORELEC CVBA**	*ENGIELBE*	*RTO*	*BE*

(*) Entity affiliated to ENGIE

CO_2 valorization

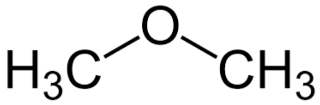
$$CO_2 + 4H_2 \longleftrightarrow CH_4 + 2H_2O$$

$$CO_2 + 3H_2 \longleftrightarrow CH_3OH + H_2O$$

$$n\,CH_3OH + H_2 \longleftrightarrow CH_3(CH_2)_{n-2}CH_3 + nH_2O$$ Gasoline

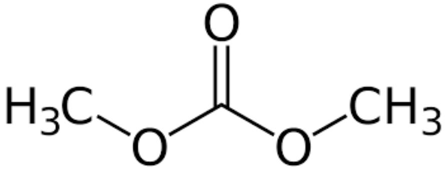
$$n\,CH_3OH + H_2 \longleftrightarrow CH_2{=}CH(CH_2)_{n-2}CH_3 + nH_2O$$ Light olefines

$$2CO_2 + 6H_2 \longleftrightarrow CH_3OCH_3 + 3H_2O$$



Dimethyl ether

$$2CO_2 + 6H_2 \longleftrightarrow CH_3OCOOCH_3 + 3H_2O$$



Dimethyl carbonate DMC

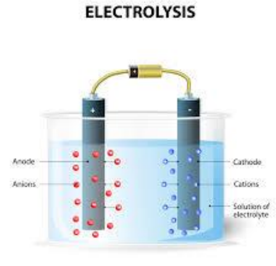
Industria del acero :Captura de CO_2 y conversion en combustibles *(C2FUEL) (June 2019 – May 2023)*

Sustainable Process Industry through Resource and Energy Efficiency

$$3C + 2Fe_2O_3 \leftrightarrow 4Fe + 3CO_2$$

7-9% de todo el CO2 producido globalmente

Water Electrolysis from renewable energy



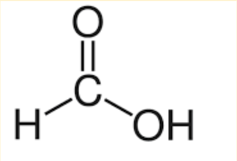
→ H_2

Blast furnace

acero gases →

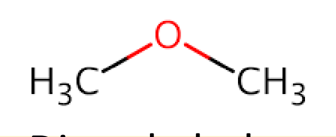
Gas Power plant

→ CO_2



Formic acid
Hydrogen Carrier

or



Dimethylether
Fuel

Technical University of Denmark

Horizon 2020
European Union Funding
for Research & Innovation

TEAM FAST

Fuel cell technology

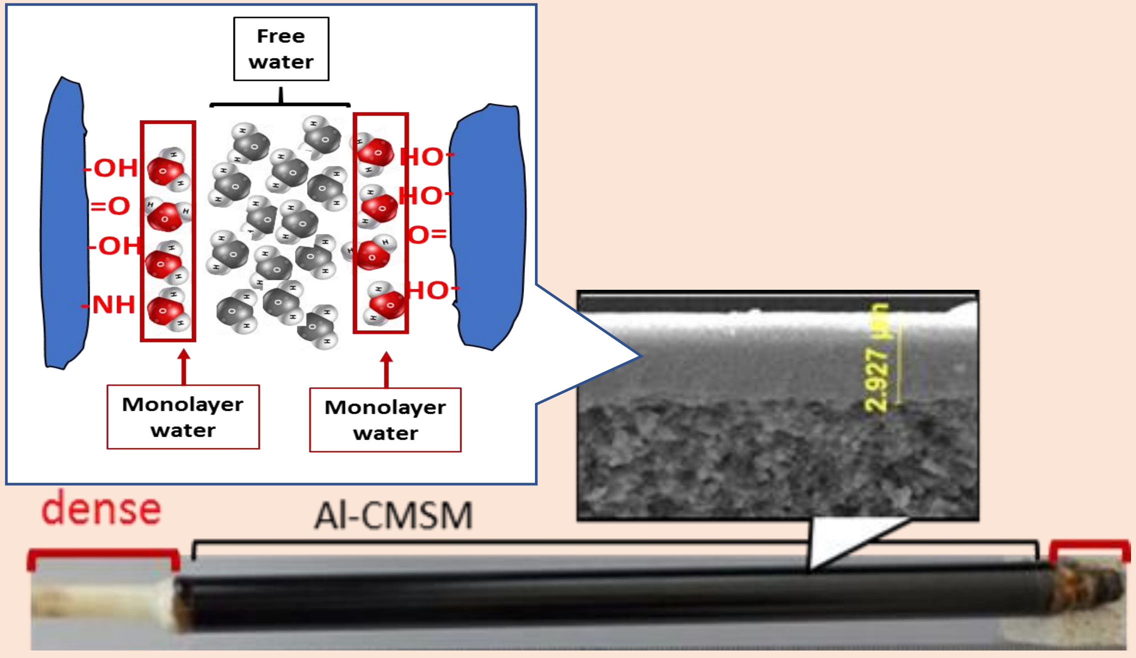
Síntesis de of dimetil-eter (DME) usando reactores de membrana

$CO_2 + 3\,H_2 \longleftrightarrow CH_3OH + H_2O$ MeOH synthesis

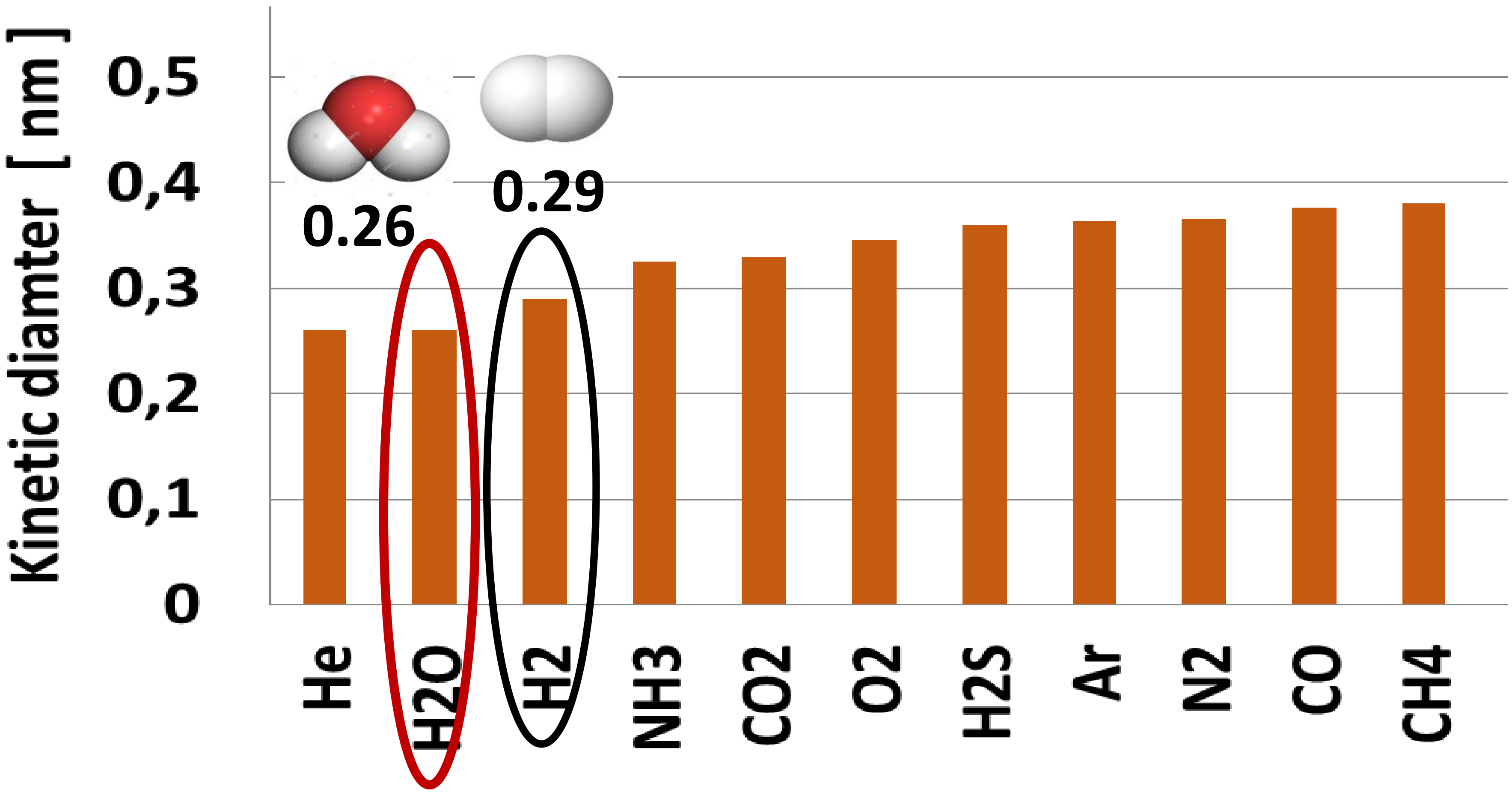
$2\,CH_3OH \longleftrightarrow CH_3OCH_3 + H_2O$ MeOH dehydration

$2\,CO_2 + 6\,H_2 \longleftrightarrow CH_3OCH_3 + 3\,H_2O$ Direct DME synthesis

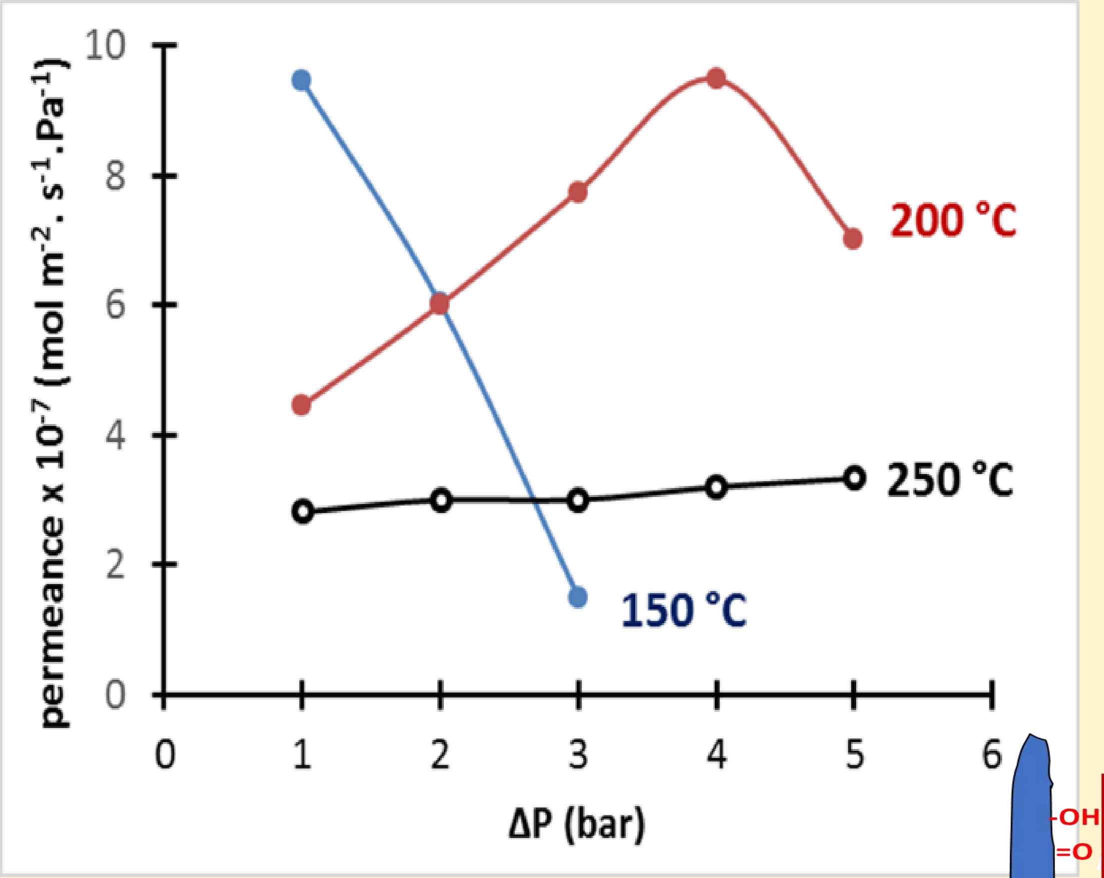
Carbon molecular sieve Water gas membrane



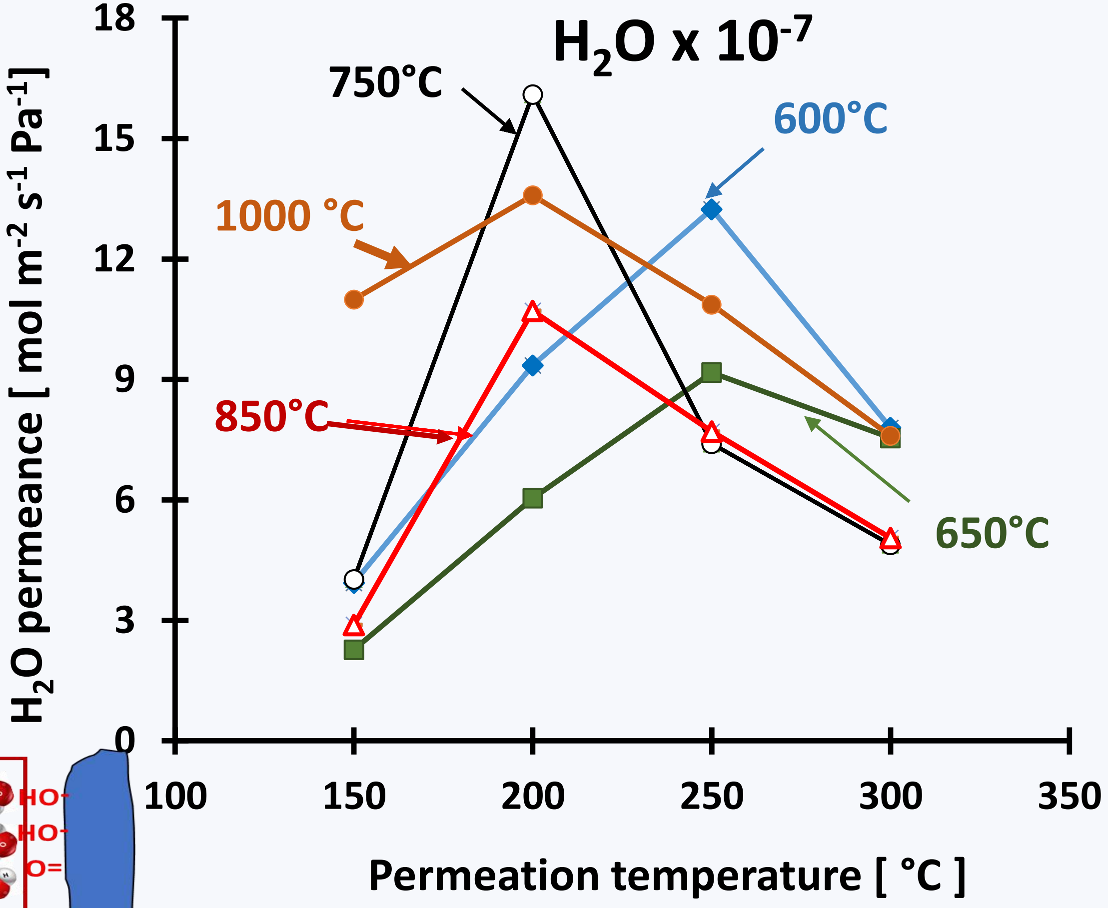
Water gas permeation membranes

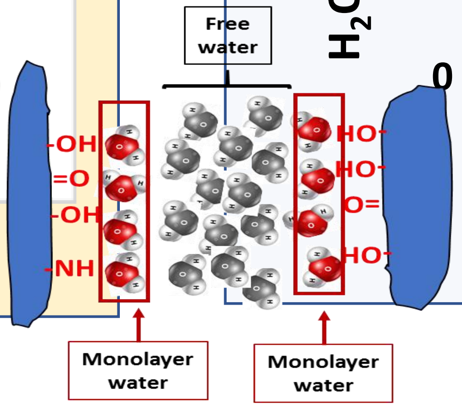


Water permeance at various pressures and temperatures

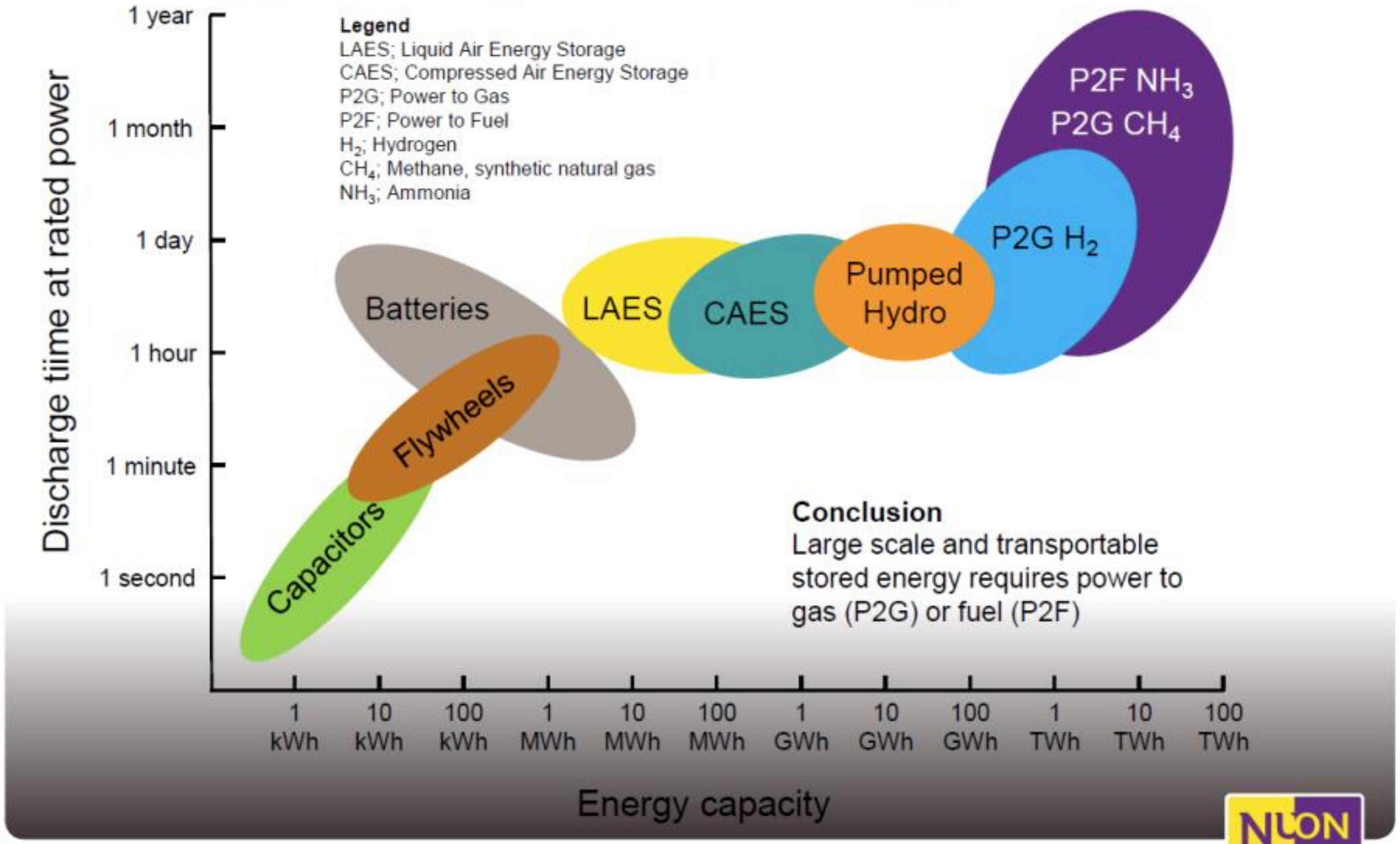


Water permeance at various permeation temperaturas in function of the carbonization temperature





Energy Storage - Technologies



CRIGEN

Saint Denis, Paris

CRIGEN es el centro de I+D corporativo de ENGIE dedicado a los gases verdes (hidrógeno, biogás y gases licuados), nuevos usos energéticos en ciudades y edificios, industria y tecnologías emergentes (tecnología digital e inteligencia artificial, drones y robots, nanotecnologías y sensores). ENGIE Lab CRIGEN lleva a cabo proyectos de I+D operativos y desarrolla pilotos, e implementa ofertas innovadoras para impulsar y acelerar la transición energética

RESUMEN

- Cambio climático está relacionado al efecto invernadero producido por el aumento de gases en la atmósfera, especialmente CO_2
- La union Europea y Japón tienen como objetivo para 2030 reducir las emisiones de gases de efecto invernadero en 40% y para 2050 en 80%
- Para 2030 aumentar en 32% la producción de energias renovables
- Hidrógeno es un combustible limpio que al ser oxidado produce agua
- Hay en el mercado autos que utilizan hidrógeno para producer electricidad usando celdas de combustible

RESUMEN II

- En el corto y mediano plazo se incrementará la producción de hidrógeno azul y verde (hidrólisis del agua)
- La electricidad producida por energía solar y eólica será barata en el futuro
- Amonia será usado como transporte de hidrógeno y como combustible
- El CO2 será convertida en .
  Gas (Power to gas. P2G) como metano o hidrógeno
  Combustibles (Power to fuels, P2F) como NH3, methanol, dimetileter
  usando hidrógeno verde

Muchas gracias

Preguntas ?