Advanced materials and Reactors for Energy storage tHrough Ammonia

https://arenha.eu/

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Index

1. Introduction

Nowadays, mankind is facing two of the most difficult challenges in its life:

- global warming and associated climate changes

- local pollution of urban areas.

1. Introduction

Energy production 21st Century

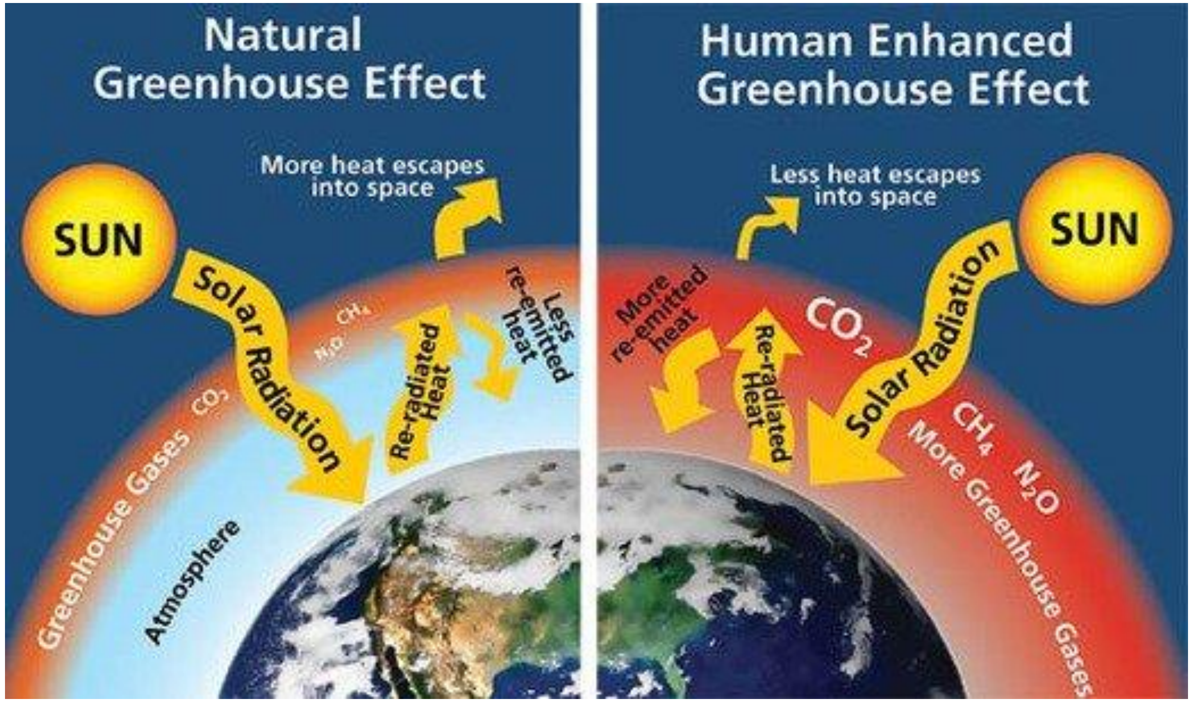
- Majority from fossil fuel derivatives (carbon based): Currently, more than 80% of global primary energy use is fossil based. Over the last decade, 85% of the increase in global use of energy was fossil based.
- CO_2 production

Greenhouse gasses

- **Effect**

  Trap IR-radiation (heat)
- **Emission CO_2**

  Natural & human activity

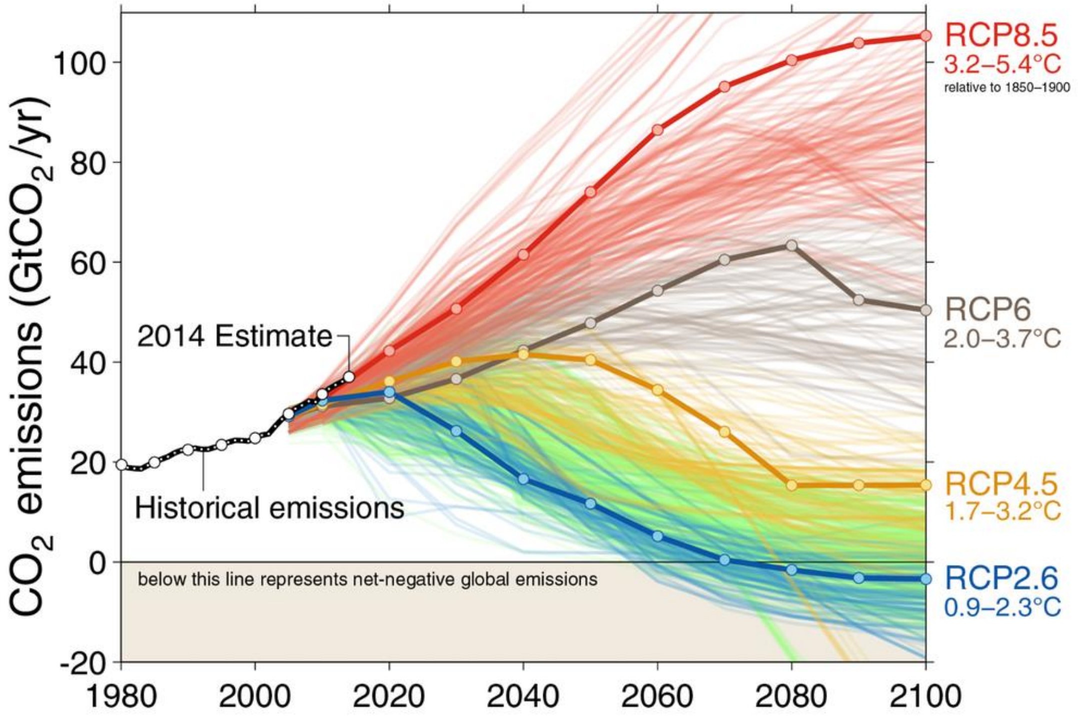


1. Introduction

The EU Commission's Low Carbon Roadmap (and the world climate contract) suggest a reduction of >80% of CO_2 emissions by 2050 compared to levels at the beginning of the 21st century.

2018: 37,1 $GtCO_2$ (www.globalcarbonproject.org)

Transition process requires a new energy system without C at the end with radical technical solutions and infrastructure investments.



Global carbon dioxide emissions from human activity, compared to four different possible futures as depicted in IPCC scenarios. Fuss et al. 2014

Climate Action in the UN's Sustainable Development Goals (SDGs): Limiting global warming to 1.5°C (https://www.ipcc.ch/sr15/)

1. Introduction

Greenhouse gases. Reduce emissions to environment.

- Increasing Energy efficiency;
- Carbon Capture, Utilizations and Storage
- Low carbon processes
- Net-negative global emission
- Search for renewable energy carrier: Hydrogen,……
- …..

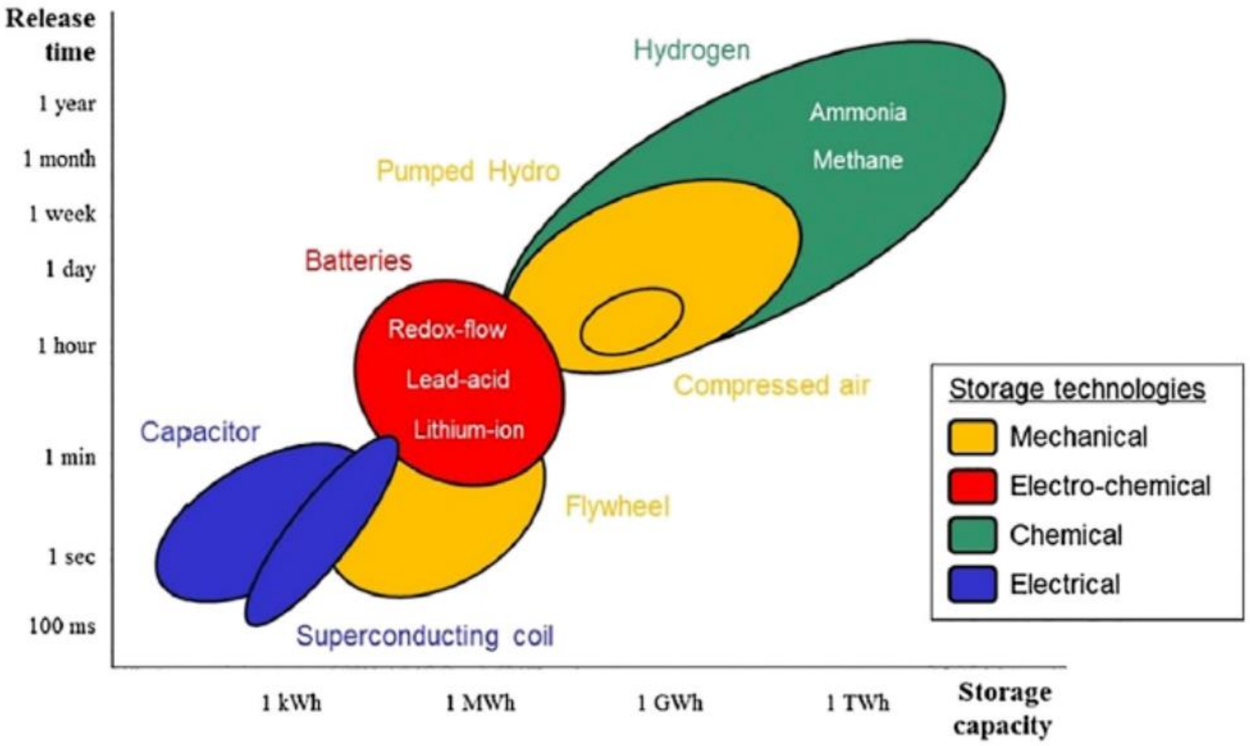
European Green Deal: Set of policy initiatives by the European Commission with the overarching aim of making Europe climate neutral in 2050.

- Maximise the deployment of renewables and the use of electricity to fully decarbonize Europe's energy supply.
- Increase renewable energy to at least 32% of the EU's final energy consumption by 2030
- By 2050, more than 80% of electricity will be coming from renewable energy sources.

1. Introduction: challenges

Renewable energy is playing an important role in addressing some of the key challenges facing today's global society, such as the cost of energy, energy security and climate change.

Energy storage technologies

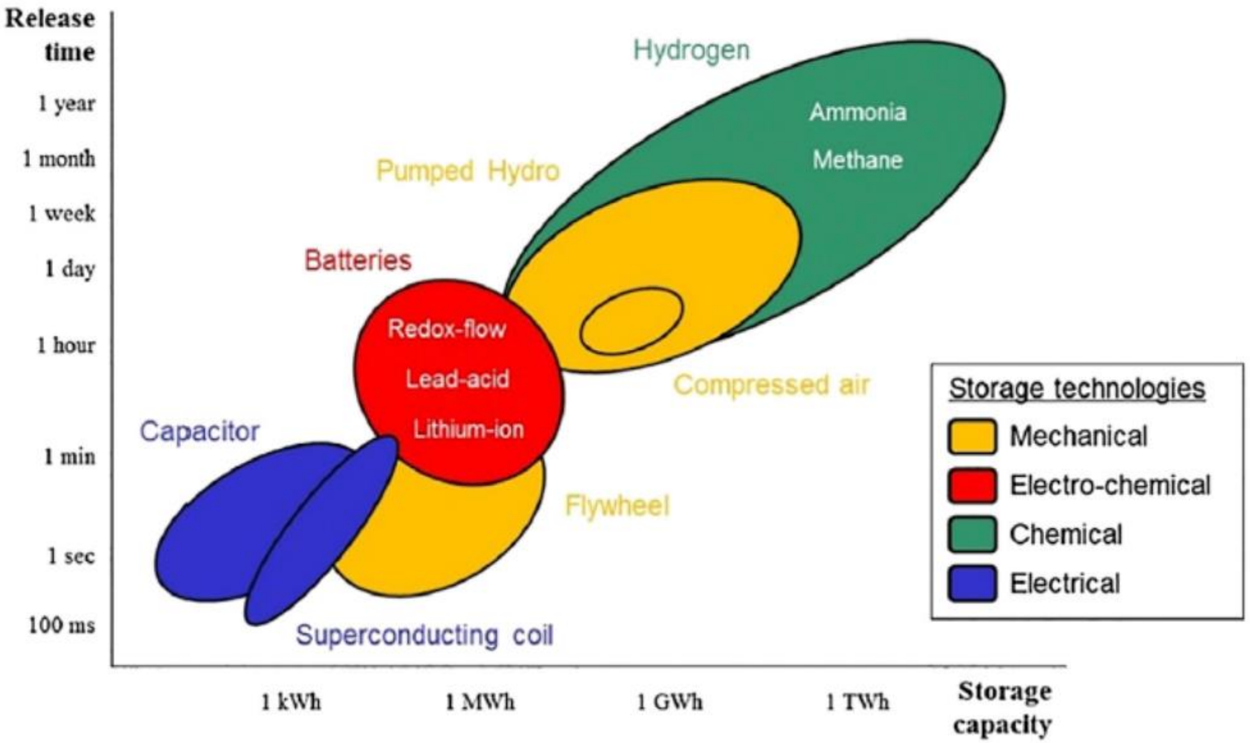


L.Ye et al. Reaction: "Green" Ammonia Production. Catalysis Vol. 3, Issue 5, p712-714, 2017
DOI: https://doi.org/10.1016/j.chempr.2017.10.016

- Sustainable energy production can only work well when the energy storage challenges are solved.
- Overcoming the inherent intermittency of renewable resources and increasing their share of generation capacity (i.e. integration of renewable energy in the grid).
- Other technologies have to be developed that can respond to these needs, and their readiness for market deployment has to be shown.
- New or improved materials for these technologies must be developed in combination with new design/architecture (i.e. improvement of electrolysers …)
- Economic competitiveness and environmental aspects have to be considered (i.e. recycling)

1. Introduction: challenges

Energy storage technologies



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- Batteries may not be the best solution to face all energy storage needs, due to cost, safety and environmental issues.
- Pumped hydro and methods such as compressed gas energy storage suffer from geological constraints to their deployment.
- Non-battery-based storage technology, such as Power-to-X technologies (Power-to-Gas, -Chemicals, -Liquids) that allows transforming renewable electricity into synthetic gases (hydrogen, methane or other gases) and chemicals/liquids, can be suitable solutions for different energy storage needs.
- The only sufficiently flexible mechanism allowing large quantities of energy to be stored over long time periods at any location is chemical energy storage: via hydrogen or carbon-neutral derivatives.
- H_2 has gained considerable attention as an ideal and clean energy carrier:
  - H_2 combustion produced only water as by-product
  - High efficiencies for energy conversion are achieved when it is employed as feedstock for power production.

2. Project overview: Objective

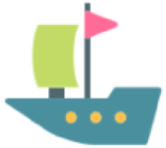
- The ARENHA project aims at using ammonia as a green hydrogen carrier and for that purpose it develops its main activities around the power-to-ammonia-to-usage value chain.
- Innovative materials are developed and integrated into ground-breaking systems enabling the flexible, secure and profitable storage and utilization of energy under form of green ammonia.
- ARENHA will demonstrate power-to-ammonia-to-usage technologies at TRL 5

Why ammonia as a H_2 carrier?

High volumetric energy density

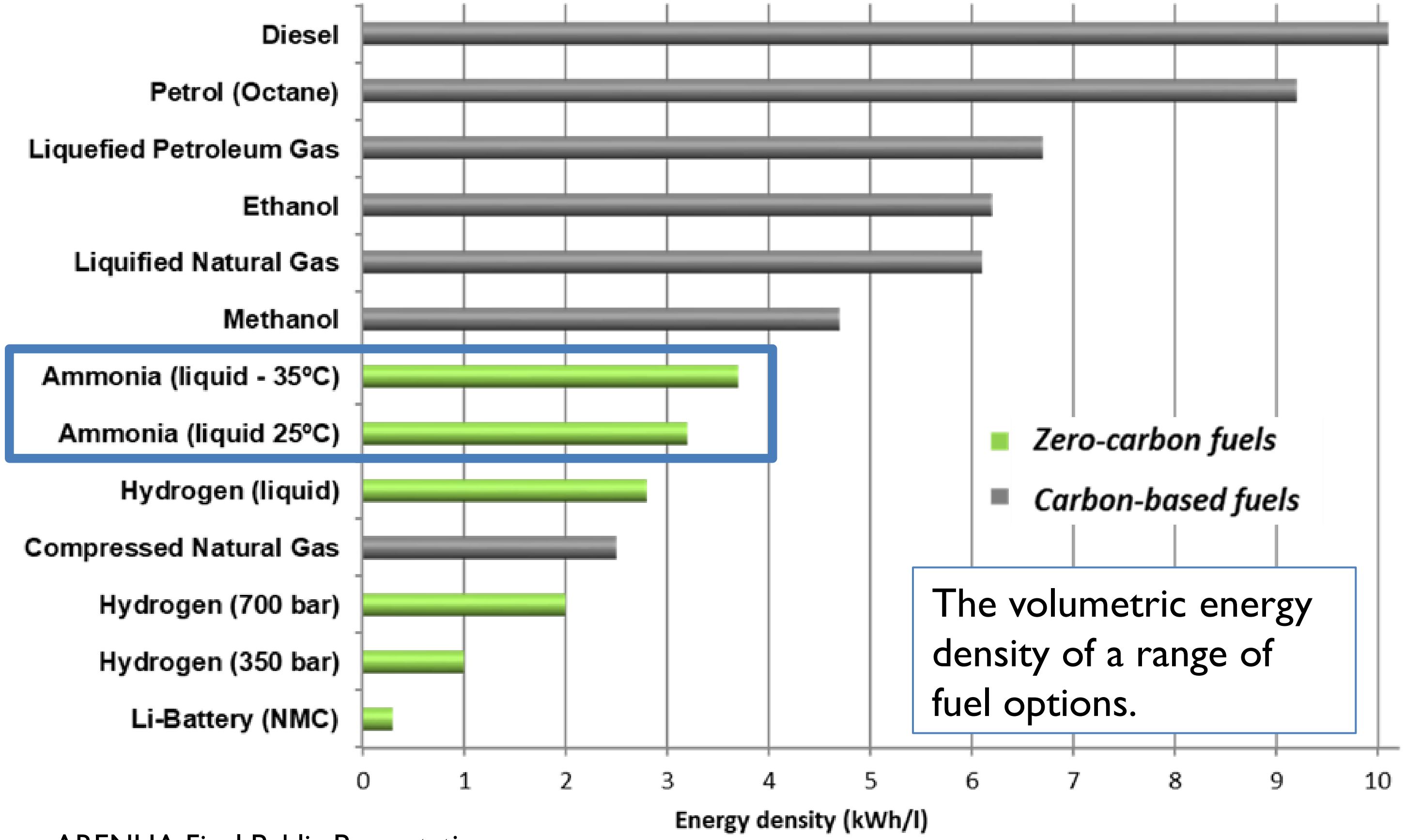
Relatively low cost

Easy to liquefy



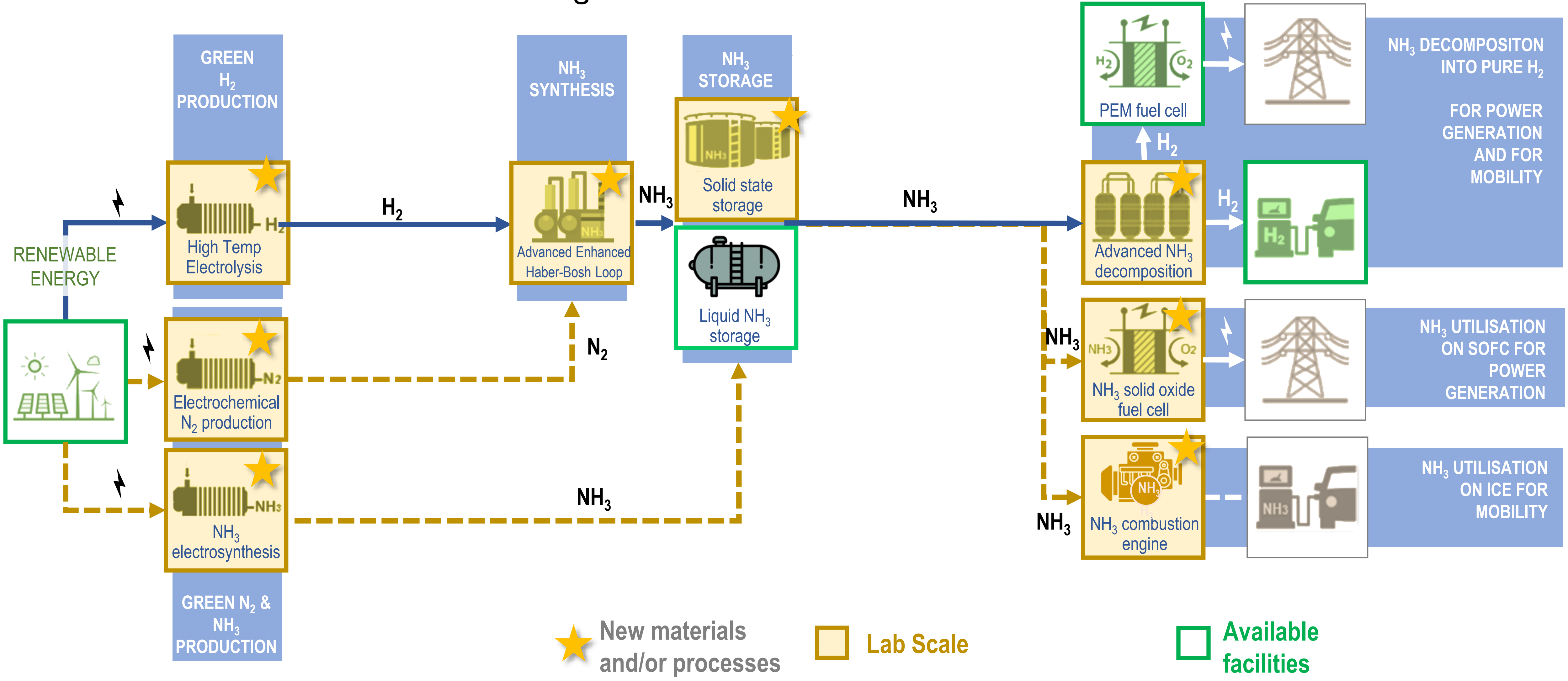
Easy to store and transport

Carbon free



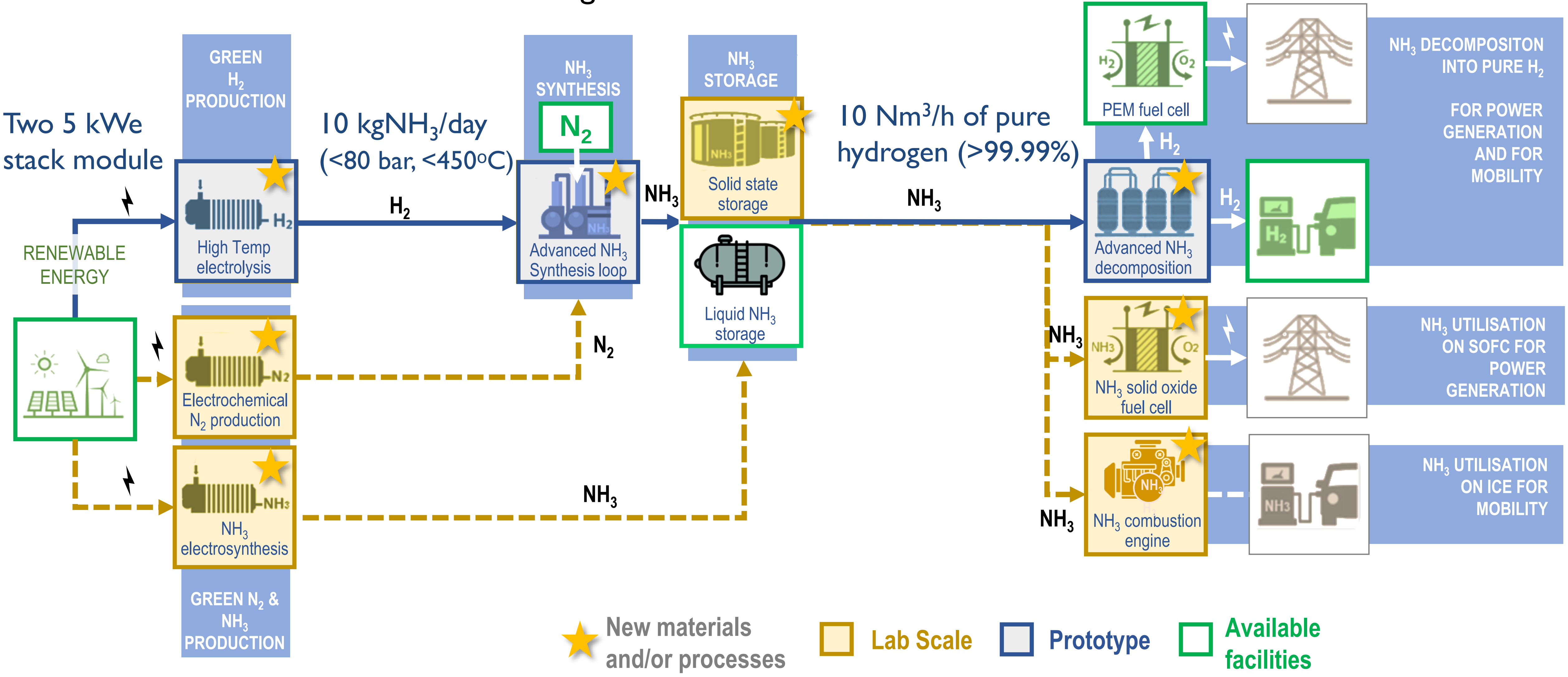
2. Project overview: Main goal and S&T targets (I)

Power-to-ammonia-to-usage value chain in ARENHA



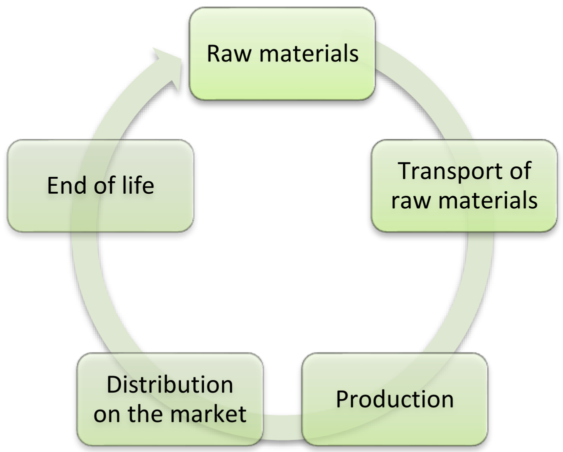
2. Project overview: Main goal and S&T targets (I)

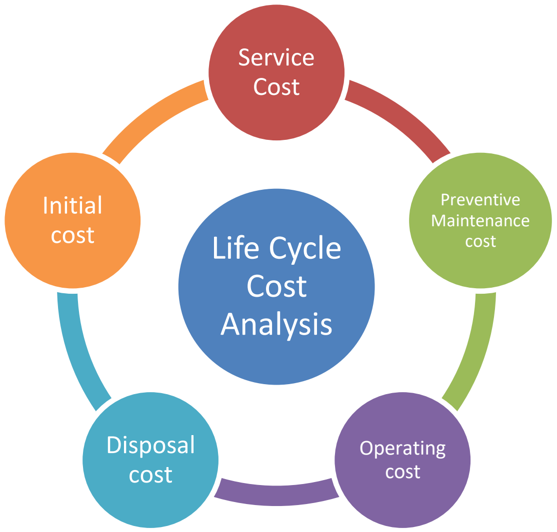
Power-to-ammonia-to-usage value chain in ARENHA



2. Project overview: Main goal and S&T targets (II)

- To assess the social acceptance, techno-economic-environmental feasibility, and replication potential of the developed value chains (LCA, LCC, LCS).





2. Project overview: Partnership

- Multidisciplinary and complementary team.
- 11 partners in 7 countries.
- Industrial oriented (45%): 5 SME/IND + 6 RTO/HES
- 3 SMEs & 2 IND

Universities

TU/e

DTU

Research institutions

tecnalia
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Centro Nacional del Hidrógeno

Fraunhofer IKTS

Science & Technology Facilities Council

Industries

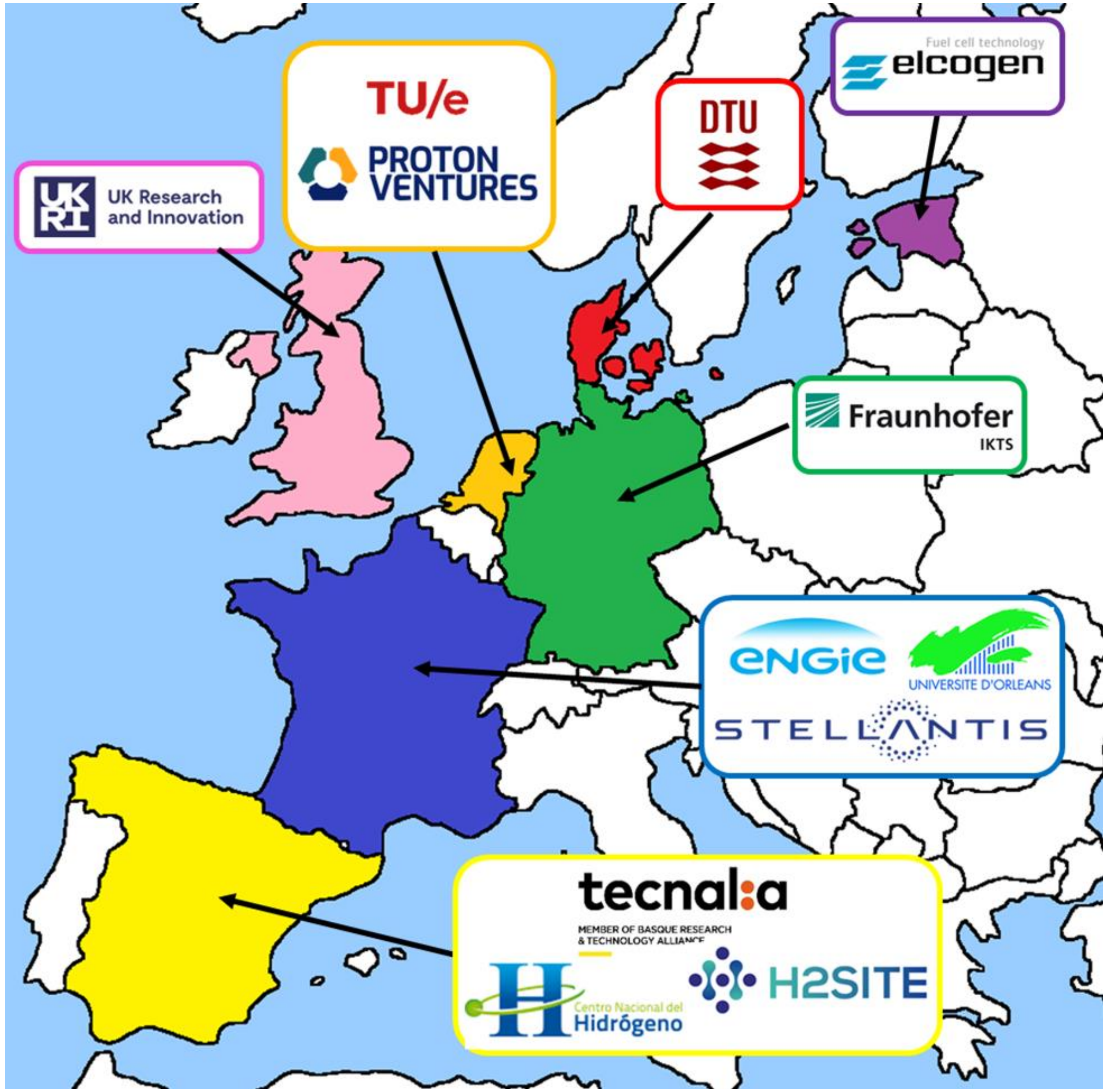
PROTON VENTURES

Fuel cell technology elcogen

H2SITE

ENGIE

STELLANTIS



2. Project overview: Approach

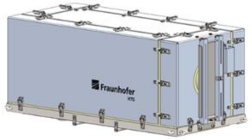
Green hydrogen production

Material development and scale up

SOEC cells and stacks

Fraunhofer IKTS
elcogen (Fuel cell technology)

Prototype manufacturing



SOEC stack modules and BoP

Fraunhofer IKTS
elcogen (Fuel cell technology)
Centro Nacional del Hidrógeno

Process, Quality Control & Recyclability

Process Control:
- Flexibility
- H2 productivity and purity
- Efficiency
- Safety

Product Control & Reciclability:
- Cell materials
- Stacks & stack modules

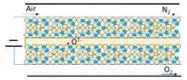
Fraunhofer IKTS
elcogen (Fuel cell technology)
Centro Nacional del Hidrógeno

Ammonia synthesis

Material development and scale up

Catalysts

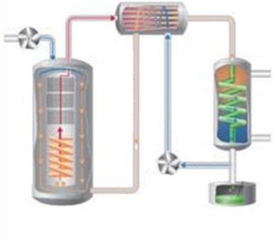
Absorbents



Electrochemical cells

UK Research and Innovation
DTU

Prototype manufacturing



Advanced Haber Bosch

PROTON VENTURES
DTU

Process, Quality Control & Recyclability

Process Control:
- Flexibility
- NH_3 productivity and purity
- Efficiency
- Safety

Product Control & Reciclability:
- Catalysts
- Absorbents

PROTON VENTURES
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Ammonia storage

Material development

Absorbents

DTU

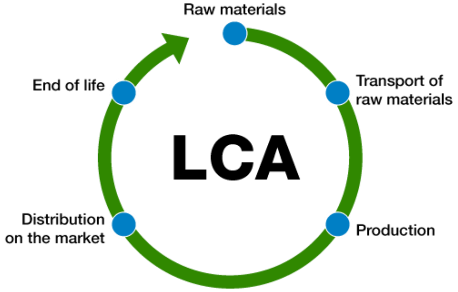
Process, Quality Control & Recyclability

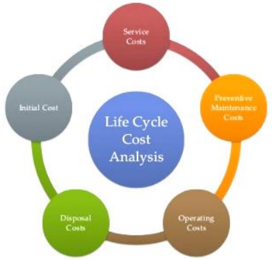
Process Control:
- Flexibility
- NH_3 productivity and purity
- Efficiency
- Safety

Product Control & Reciclability:
- Absorbents

DTU

2. Project overview: Approach





safety

ENGIE
Centro Nacional del Hidrógeno

Ammonia Decomposition

Material development and scale up

Catalysts

Advanced Membranes

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Prototype manufacturing

Membrane reactor

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Process, Quality Control & Recyclability

Process Control:

- H_2 productivity and purity
- Efficiency
- Safety

Product Control & Reciclability:

- Catalysts
- Membranes

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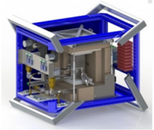
Ammonia usage

Benchmarking of novel technologies



SOFC NH_3

NH_3 combustion

Fraunhofer IKTS
STELLANTIS
UNIVERSITE D'ORLEANS

System integration and Demonstration

Overall System

- H_2 production
- NH_3 Synthesis
- NH_3 Storage
- NH_3 Decomposition

Fraunhofer IKTS
ENGIE
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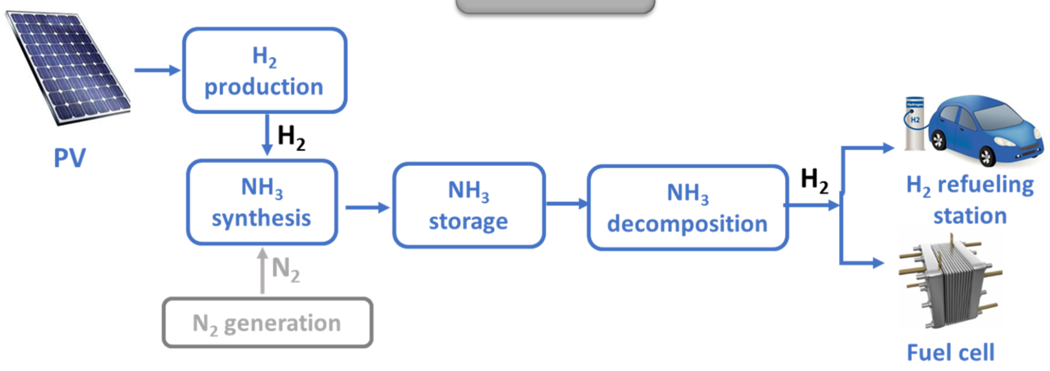
PROTON VENTURES

System Demonstration



Centro Nacional del Hidrógeno
ENGIE

2. Project overview: Impact

More efficiently and cheaper long-term energy storage in form of green ammonia

Hydrogen carrier:
Mobility, transport and industry decarbonisation

Increasing renewable shares in the grid with large scale energy storage.

Strategic European leadership in energy storage.

Decrease energy import dependency by using ammonia to diversify energy supply (i.e. H_2) from third countries

- Alternative energy import through renewable electricity storage and long-distance transportation.
- Secure and clean supply of renewable energy

Support to the clean energy transition / European Green Deal.

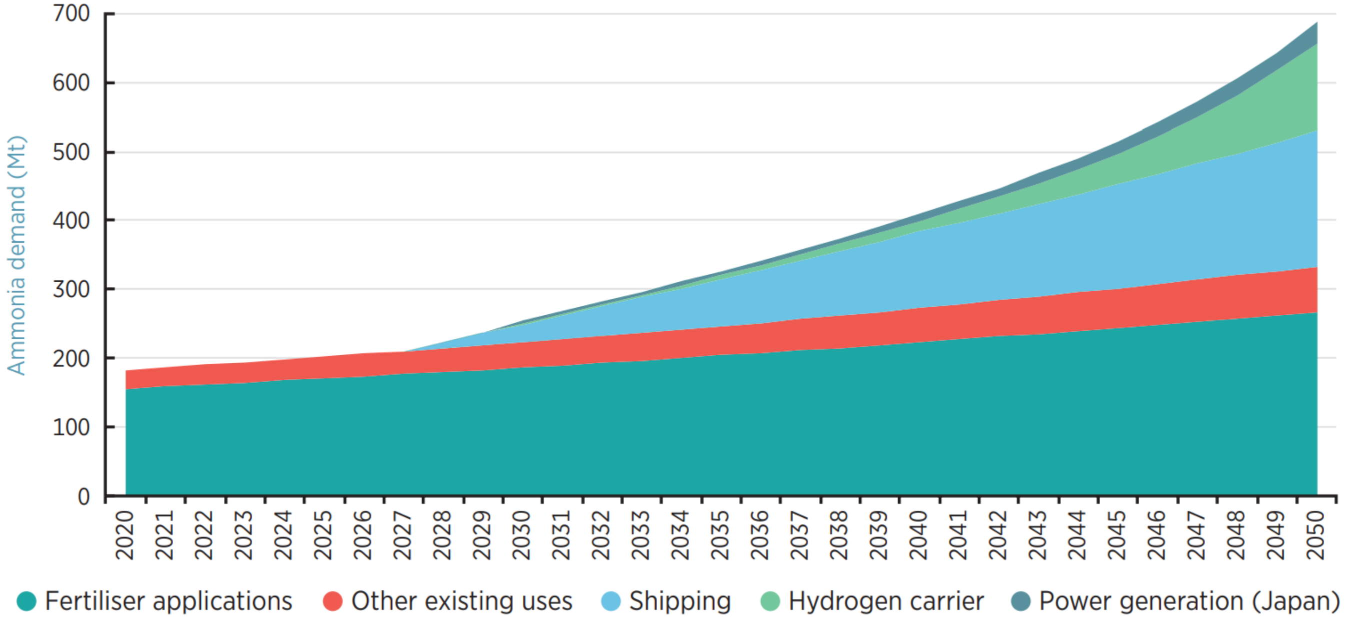
- Low carbon society using hydrogen.
- Replace natural gas, coal and oil in hard-to-decarbonise industries and transport sectors (i.e.; maritime).
- Reducing the amount of CO_2 emissions.

3. Business case definition

Market analysis

Objective: Analyse markets, stakeholders, and their needs.

- Current market and Future market with new usages
- Expected stakeholders markets for ARENHA's technologies
- Sterns and market drivers



Expected ammonia demand up to 2050 for the 1.5° C scenario. IRENA, 2022

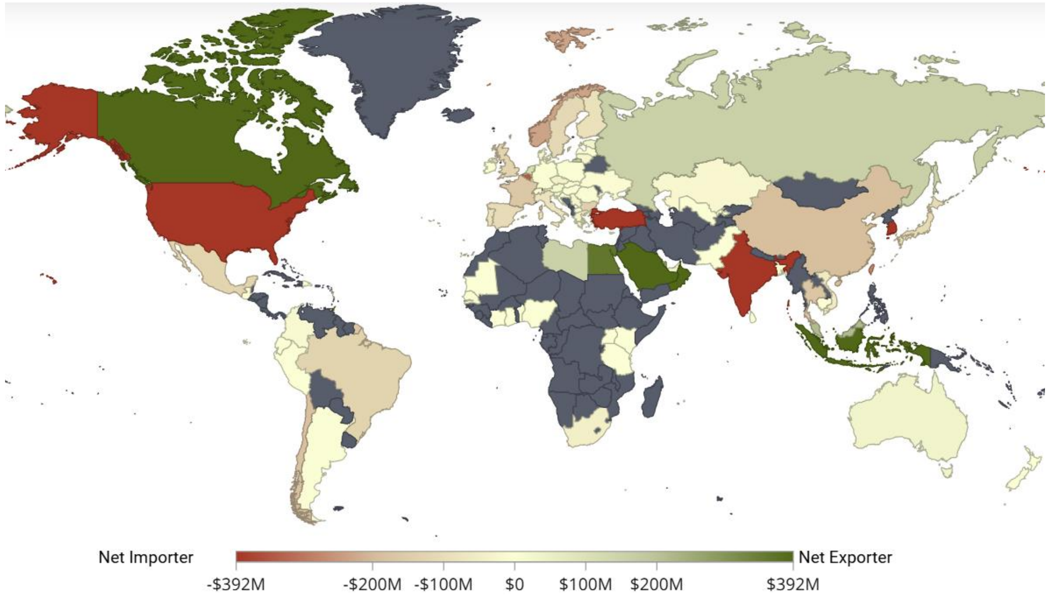
Key Insights from the market analysis:

- Renewable energy at hundreds of GWs per year scale
- Carbon price to incentivize investment
- Subsidies to mitigate investment risk
- Regulation to set timeline (ReFUEL, IMO example)
- Economies of scale: Electrolysis scale-up to reduce costs
- Certification and compliance to mitigate competition.

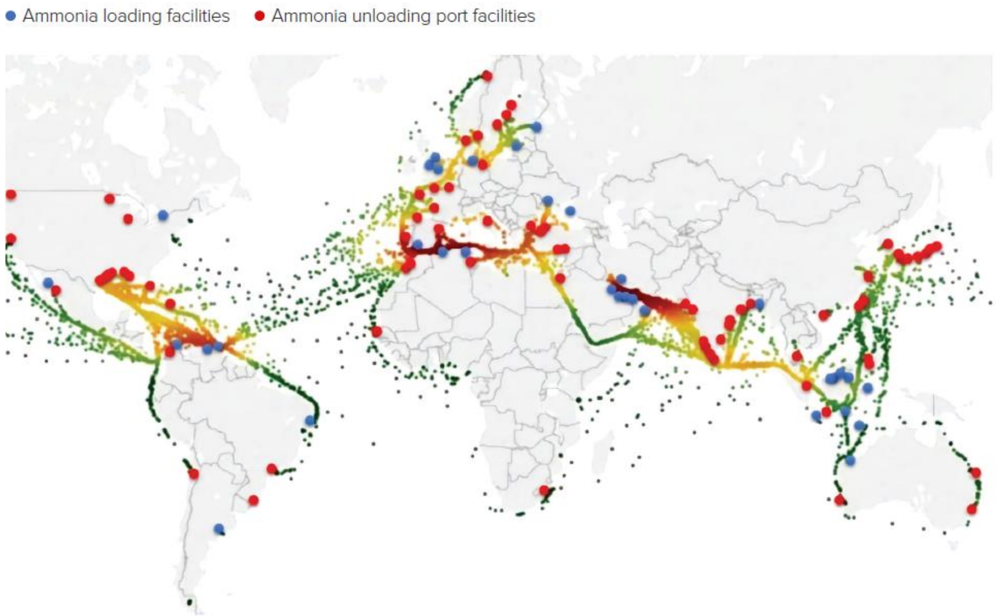
3. Business case definition

Activity 1: Market analysis

Ammonia trade



Anhydrous ammonia Product trade, Exporters and Importers in 2023 | Source: Observatory of Economic Complexity



Ammonia shipping infrastructure in 2017 , including a heat map of liquid ammonia carriers and existing ammonia port facilities. | Source: The Royal Society

Main Exporters:

- Trinidad and Tobago (18.6%), Saudi Arabia (15.3%), Indonesia (10%) and Canada (8.85%)

Main Importers:

- US (15.2%), India (13.6%), Morocco (9.75%), Turkey (4.81%) and China (3.51%)

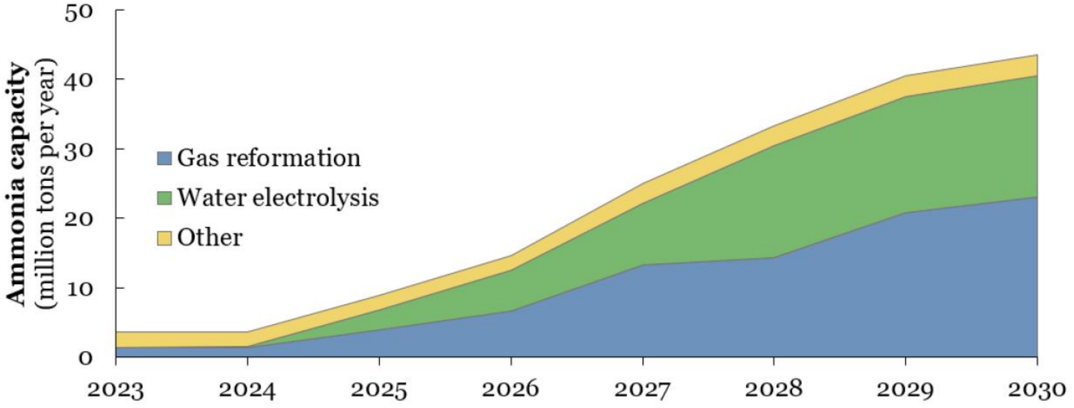
Existing ammonia trading infrastructure can support low-carbon ammonia exports

3. Business case definition

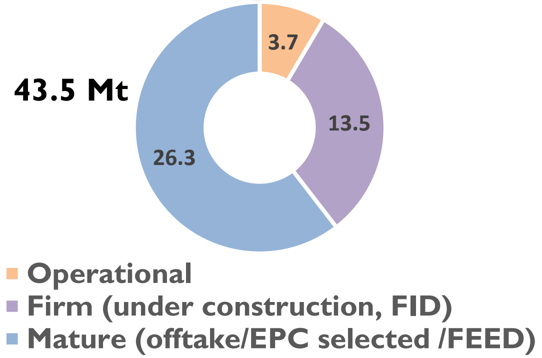
Activity 1: Market analysis

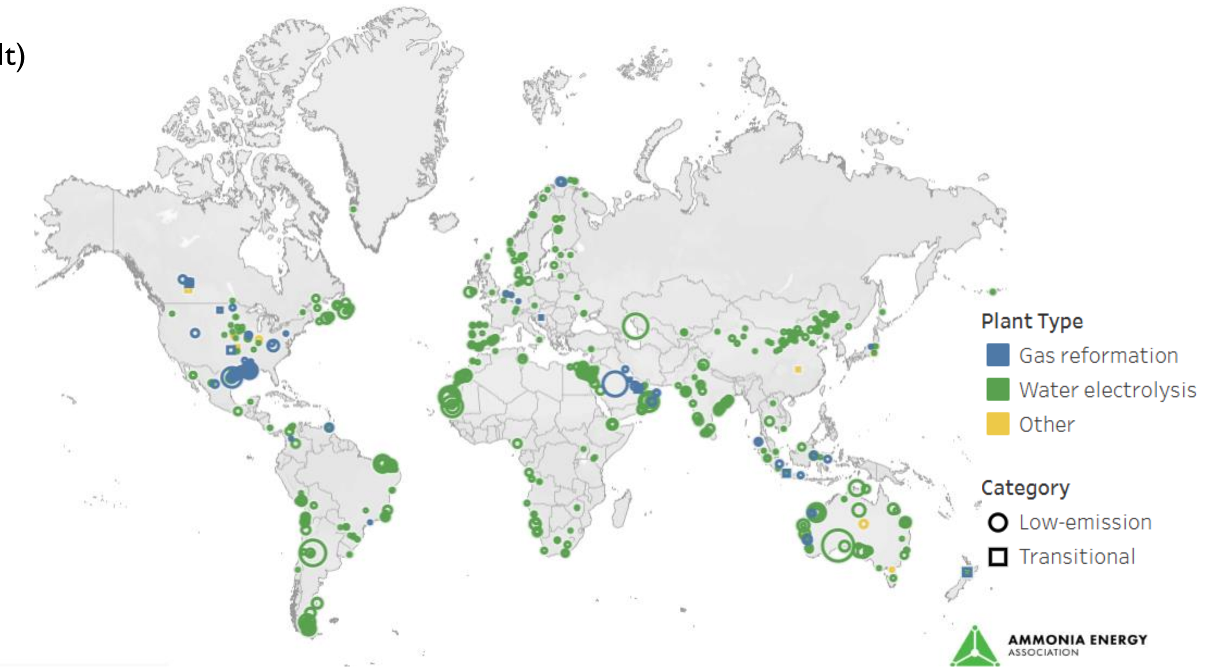
Low carbon ammonia supply

- **485** Ammonia projects (Feb. 2025) from 102 (Dec. 2022) for a total **451.2** millions tons (Mt)
- 43.5 Mt ammonia capacity could be operational by 2030, **37.7 Mt** low-carbon (~90%)



Operational, firm and mature Low-carbon ammonia projects. | Source: Ammonia Energy Association





Low-carbon ammonia project based on natural gas (blue) set to lead near term supply compared to electrolysis based (green) ammonia projects

- High financing cost and low offtakers willingness to pay is a barrier for green ammonia project developments

Need of **affordable** and **cost-effective** green ammonia production technologies to move more projects towards Final Investment Decision (FID)

3. Business case definition

Activity 2: Value proposition

Objective:

1. **Show value** of technology for **energy storage**
2. Demontrate **uniqueness** and **market impact** (benefits and competitive edge)

How:

1. **Characterize** KERs
2. Evaluate **impacts** on customers
3. **Create a value map**

Exploitable Results:

Goal: Determine and characterize the IP that can be exploited

21 exploitable results identified and characterized

- **6 Key Exploitable Results** (KER)
  - linked to the 3 prototypes
  - used for the business models
- **15 other exploitable results**:
  - linked to the other work in ARENHA

3. Business case definition

Activity 2: Value proposition

Key Exploitable Results:

Nº	Exploitable Result	Lead Partner
KER1	H_2 supply for ammonia applications	ENGIE
KER2	Advanced Electrolyte Supported Cell SOEC electrolyser for renewable hydrogen production	IKTS
KER3	Advanced Cathode Supported SOEC electrolyser for renewable hydrogen production	ELCOGEN
KER5	Advanced ammonia synthesis unit	PV
KER6	Advanced ammonia decomposition membrane reactor using DS Pd-based membranes	H2SITE
KER11	Software tools for membrane reactor design	TUE

3. Business case definition

Activity 2: Value proposition

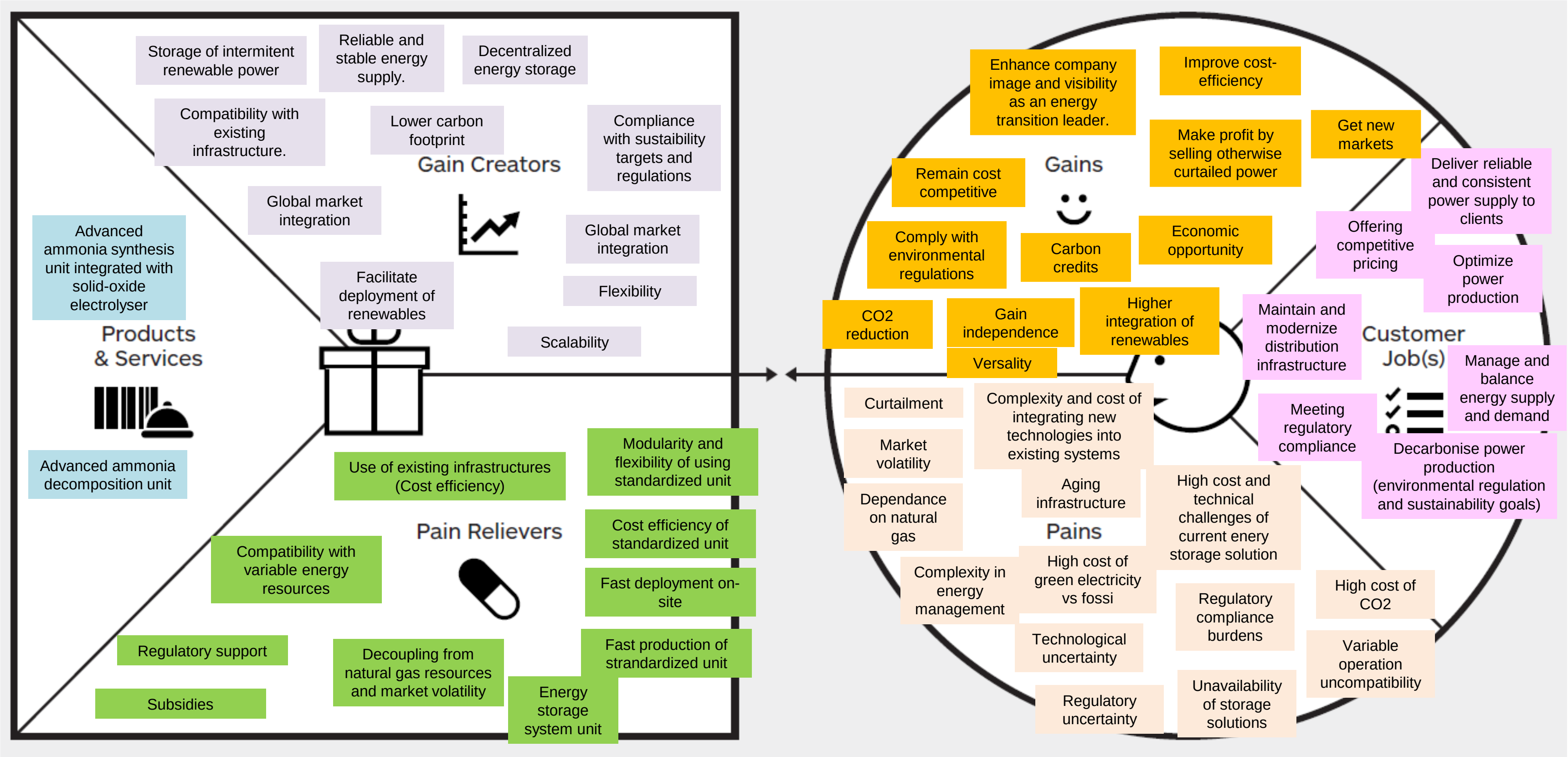
Value Map:

Goal: Elaborate a value proposition canvas (value map) for the business model

1. Define customer profiles
Describe Jobs (need to get done), pain points & desired outcomes.

2. Map value creation
Visualize how ARENHA solution eases pains and delivers key benefits

3. Validate fit
Use customer feedback to align your offer with real market needs.



ARENHA Value Proposition ***Power companies and Energy as Service companies***

Value Proposition Canvas of ARENHA products.

3. Business case definition

Activity 4: Business Model and Go-to-Market Strategy

Objective:

Maximize commercial impact of ARENHA results

How:

1. Develop Business Plan
2. Define a Go-to-Market strategy

Questions we ask:

1. How do we best use the project's exploitable results to build a business?
2. What is the final business model selected for the commercial exploitation of the ARENHA results?
3. How will the business generate revenue?
4. What products or services will generate revenue?

Business model:

- A final business model (BM) was selected based on market analysis and characterization of the key exploitable results (KER)
- The final BM is ***Energy storage unit for power, energy service and oil & gas companies*** divided in 2 sub-BM:
  - ***BM1: Power to ammonia***
  - ***BM2: Ammonia to power***
- The Business Model Canvas (BMC) approach was adopted to characterize the entire business, including customers, revenues, cost structure and key activities.

3. Business case definition

Activity 4: Business Model and Go-to-Market Strategy

Go-to-Market strategy (GTM):

- Commercialization and GTM strategy are crucial steps in launching a new product or service to the market.
- GTM help a business introduce its offering to potential customers, build brand awareness and generate sales.
- Outlines how to leverage direct or indirect marketing, sales, logistics and distribution channels to deliver ARENHA's solutions to target customers, aiming to maximize sales efficiency and profitability.

The GTM strategy for a startup differs significantly from that of an established company. For startups, the focus is on attracting early adopters rather than the broader market.

The GTM strategy includes:

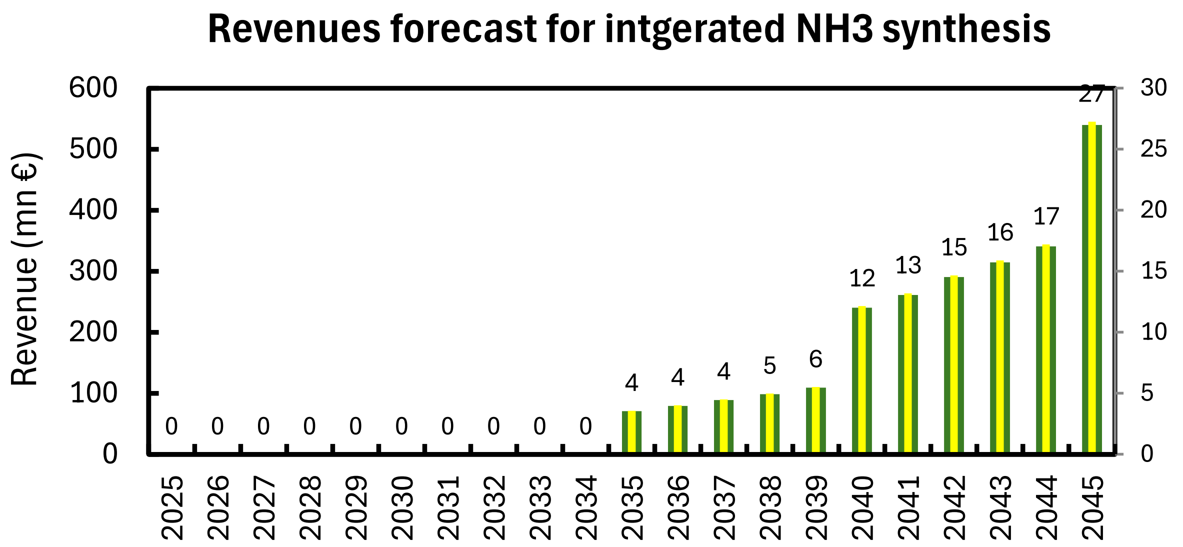
- Product description and value proposition
- Identification of competitors
- Positioning
  - Market role and differentiation
  - Positioning and long-term vision
- Risk and mitigations
- Teams
- Timeline and Milestone for:
  - Technology development and deployment
  - Entering market
- Pricing strategy
  - Pricing model
  - Pricing structure
- Distribution channels and sales strategy
- Revenue projections and monetization strategy

Activity 4: Business Model and Go-to-Market Strategy

Approach for revenues projection:

1. Forecast ammonia demand in Europe
2. Assume market penetration
3. Determine Serviceable Market
4. Determine number of units sold
5. Production cost of 1 unit (60 TPD) = X1 M€
6. Sale price of 1 unit = X2 M€
7. Revenues projection
   - First sales are projected for 2035.
   - Projections span from 2035 to 2045.

Market Penetration (Assumption)
- 1% penetration from 2035 to 2039.
- 2% penetration from 2040 to 2044.
- 3% penetration in 2045.



4. Green hydrogen production

System requirements, design and modelling

Objectives

- Define the industrial requirements for green hydrogen production units based on Solid Oxide Cell Electrolysis (SOEC) technology
- System modelling, process design and simulation
- Modelling and simulation of the integrated Power-to-Ammonia solution
- Techno-economic analysis and comparison with benchmark technologies to assess technology potential

4. Green hydrogen production

System requirements, design and modelling

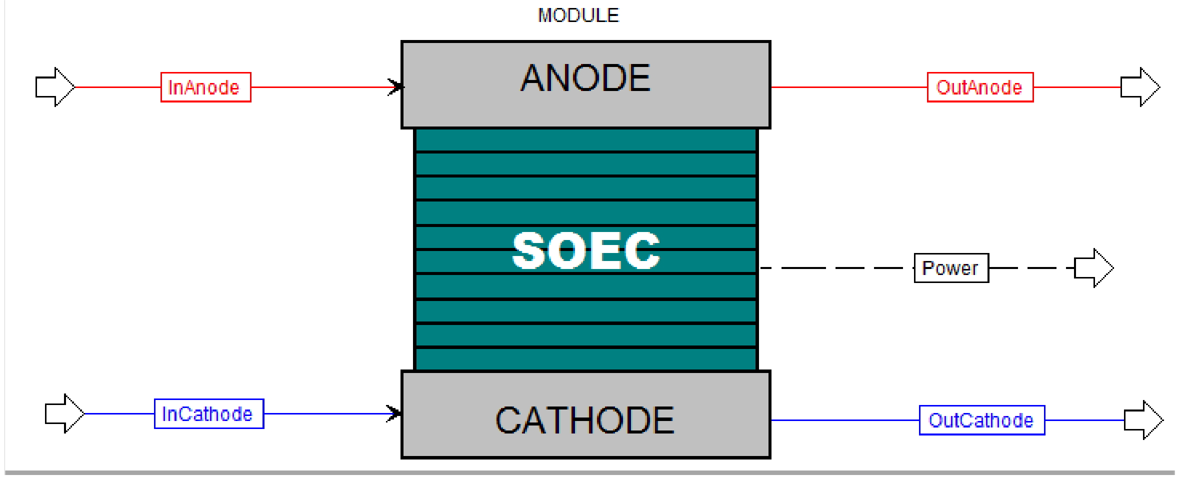
Industrial requirements

- The process parameters for the ARENHA process have been defined;
- Mass and energy balance of each individual process unit were conducted to define the inputs and outputs parameters of each process block.

System requirements, design and modelling

SOEC electrolysis modelling

- Review of SOEC model with various level of complexity (from 0D to 2D);
- Identification of key experimental parameters required for lumped model definition;
- SOEC 0D stack model developed (Aspen Custom Modeler) and validated with experimental data from FhG-IKTS and Elcogen

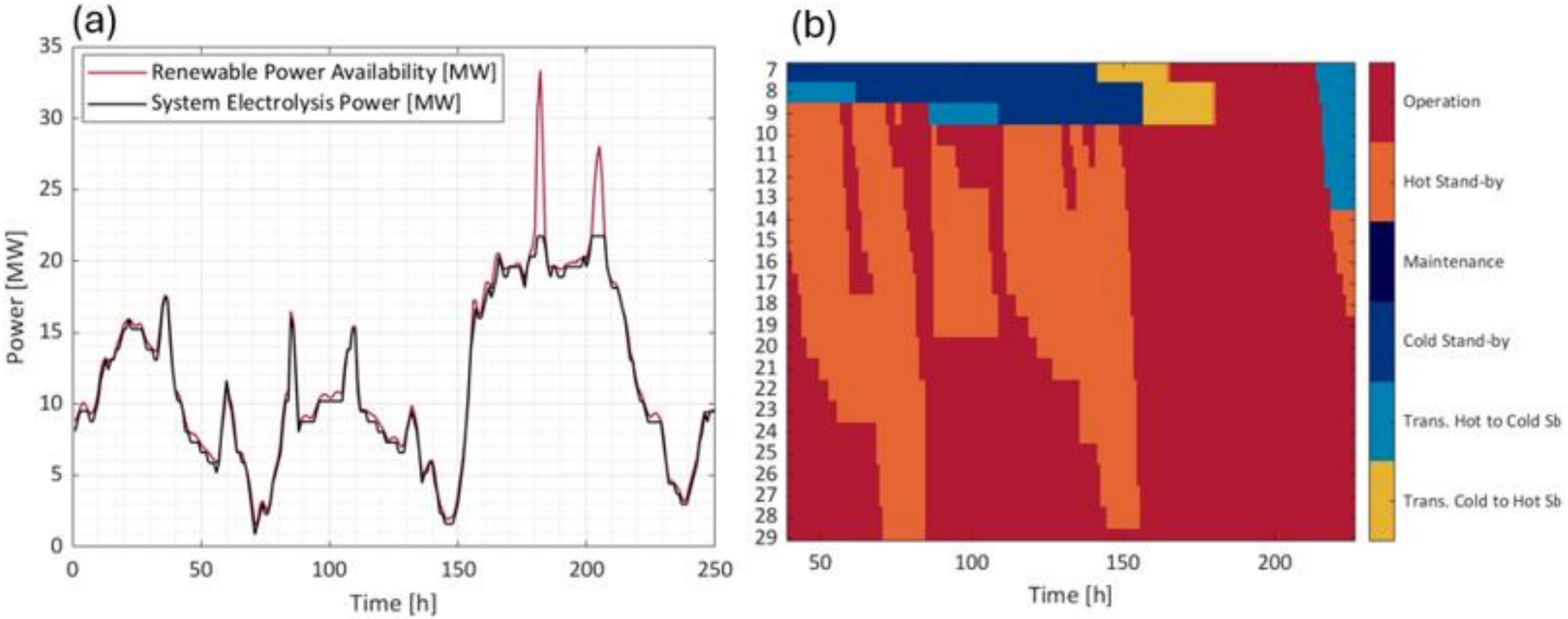


4. Green hydrogen production

System requirements, design and modelling

SOEC electrolysis modelling

- Implementation of Stack Model with system balance of plant model (Aspen Plus)
- Development of a dynamic state model for modular Solid Oxide Electrolysis Systems (MATLAB)
- Process simulation with intermittent power sources;

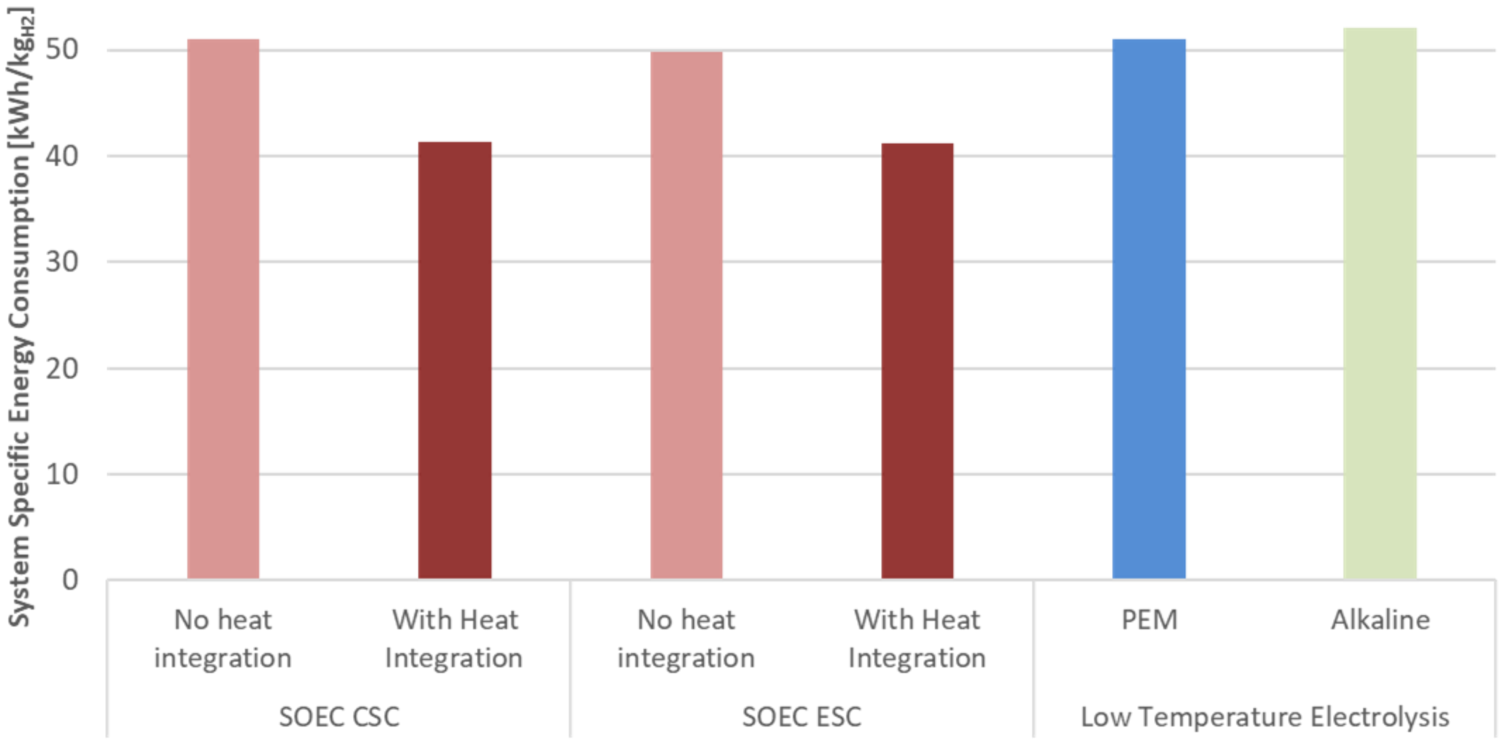


(a) Electrolyser Energy utilisation. (b) Electrolyser Modules operation.

System requirements, design and modelling

SOEC electrolysis modelling

- Evaluation of System Key Performance Indicators and benchmarking with low-temperature electrolysis technologies. Assessment of the potential, the strengths and the weaknesses of the full-scale plant.



System requirements, design and modelling

Conclusions

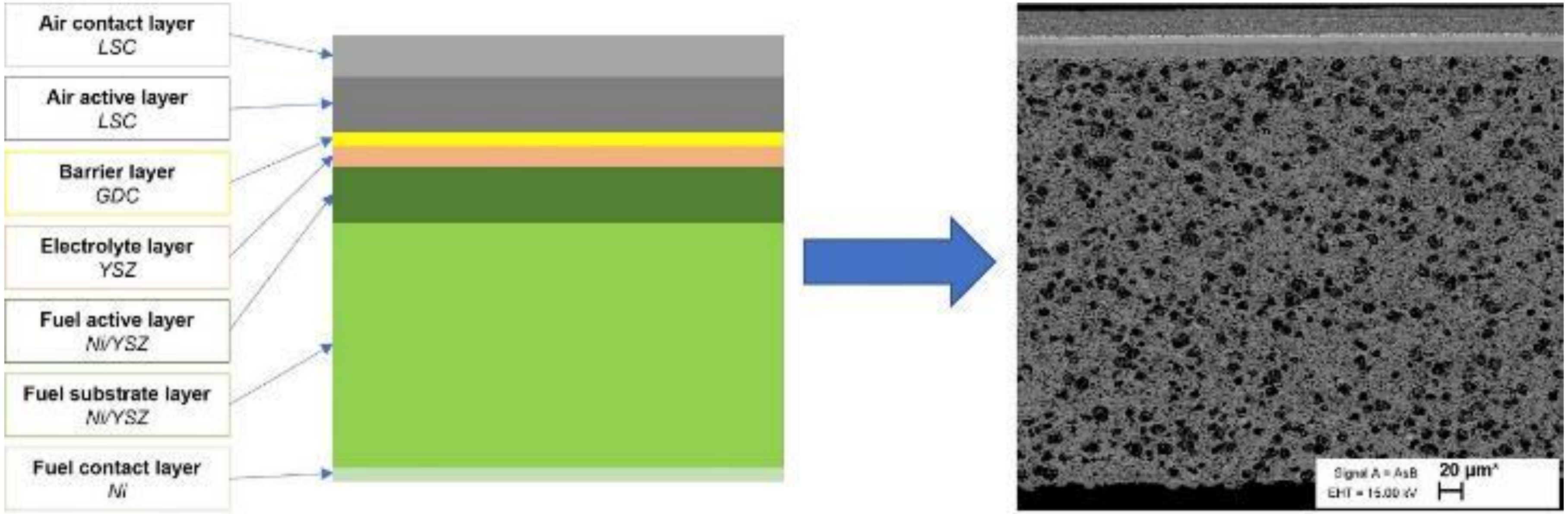
- Development of a model, validated with experimental data, for the estimation of Solid Oxide Electrolysis systems operation, performances and costs;
- Despite disadvantages related to lower TRL and high temperature of operation, Solid Oxide Electrolysis technology allows for higher efficiency hydrogen production with the potential to compete with Low-T electrolysis technologies, especially for e-fuels (i.e. ammonia) production applications.

4. Green hydrogen production

SOEC development

Development of modified cathode supported cells for SOEC (Elcogen)

- The state-of-the-art SOFC is not optimized for electrolysis operation at high current density.
- New materials and microstructural changes in the air active layer and fuel active layer have been explored to optimise cell for SOEC mode.
- New SOECs has been manufactured incorporating all the findings and then assembled in stack to be tested in a 5kW system for validation.



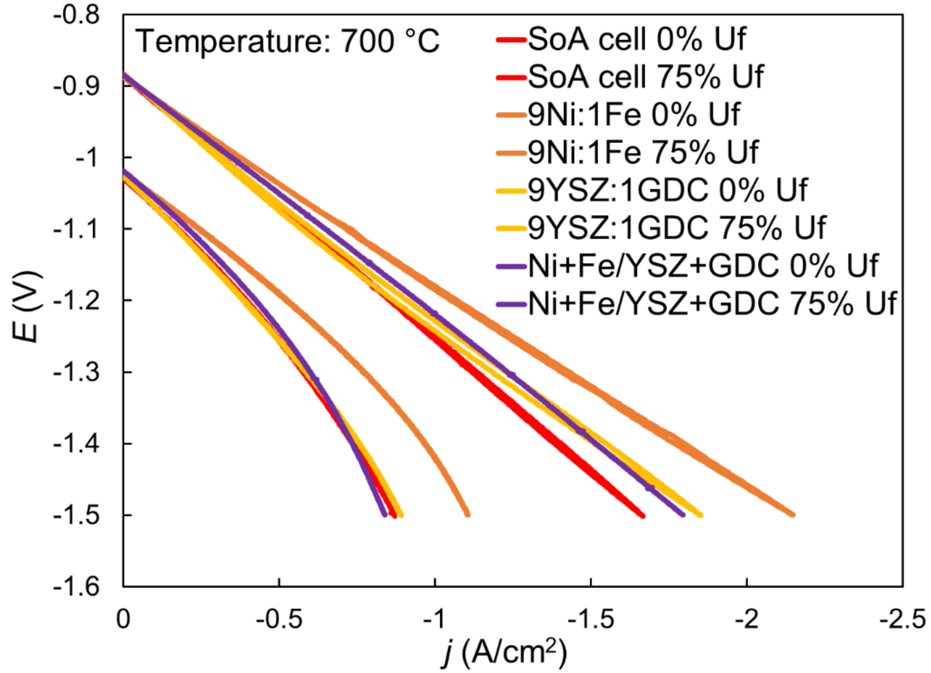
Schematic representation (left) and polished SEM cross-section (right) of a State-of-the-Art Elcogen commercial cell.

SOEC development

Development of modified cathode supported cells for SOEC (Elcogen)

- Development of new Elcogen SOEC cell designs:
  - New materials in the hydrogen electrode active layer.
  - Changes to hydrogen electrode active layer microstructure.
  - New materials in the air electrode layer.

- Results:
  - Modifications to hydrogen active layer with positive results:
    - Ni-Fe/YSZ
    - Ni/YSZ-GDC
    - Ni-Fe/YSZ-GDC
    - Thicker active layer

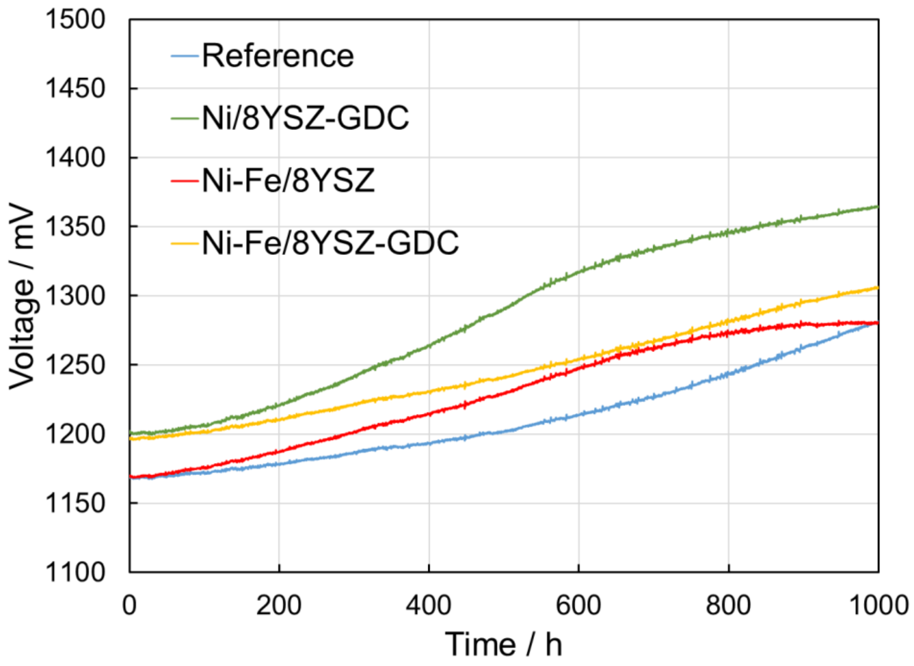


Single button cell performance test results at high and low fuel utilization

SOEC development

Development of modified cathode supported cells for SOEC (Elcogen)

- Validation of new materials in single cell tests in a stack environmer
  - The Ni-Fe/YSZ active hydrogen electrode gave best results:
    - Faster stabilization
    - Stabilized by the end of the 1000-hour test.
    - Comparable performance with reference cells
  - Choice for the E1500 demo stack:
    - Ni-Fe/YSZ hydrogen electrode active electrode
    - Thicker hydrogen electrode active layer



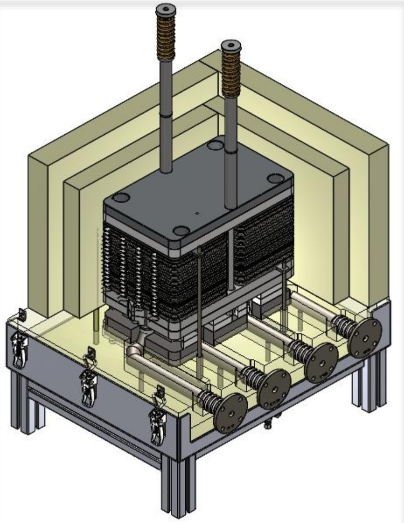
Short stack test results with the most potential cells

4. Green hydrogen production

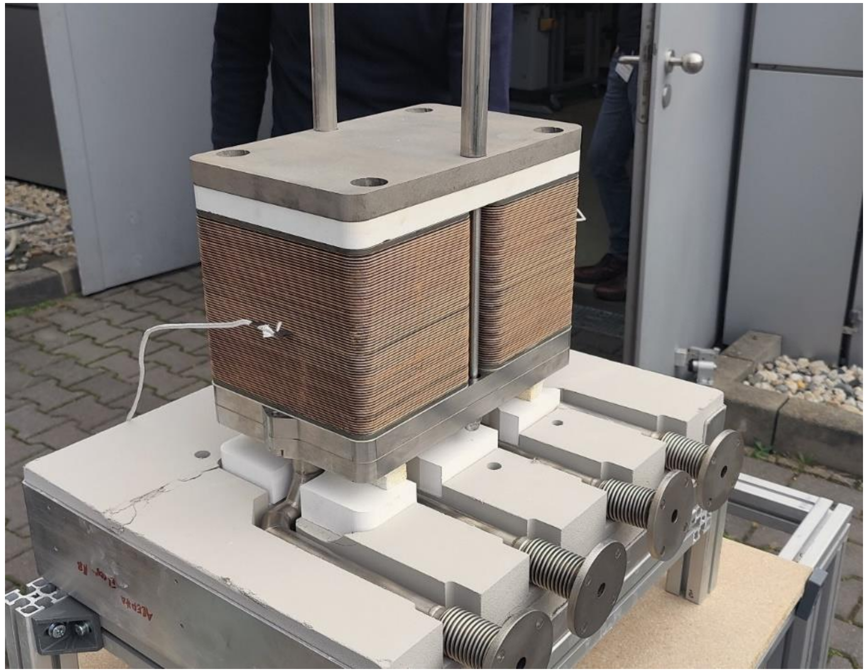
SOEC Elcogen protype

E1500 Stack module design, assembly and test

- Assembly of the 5-kW demo stack with Elcogen stacks.
- Successfully integrated into module by FhG-IKTS
- Test at test rig ongoing



Elcogen SOEC stack module



Demo stack during integration into the module

4. Green hydrogen production

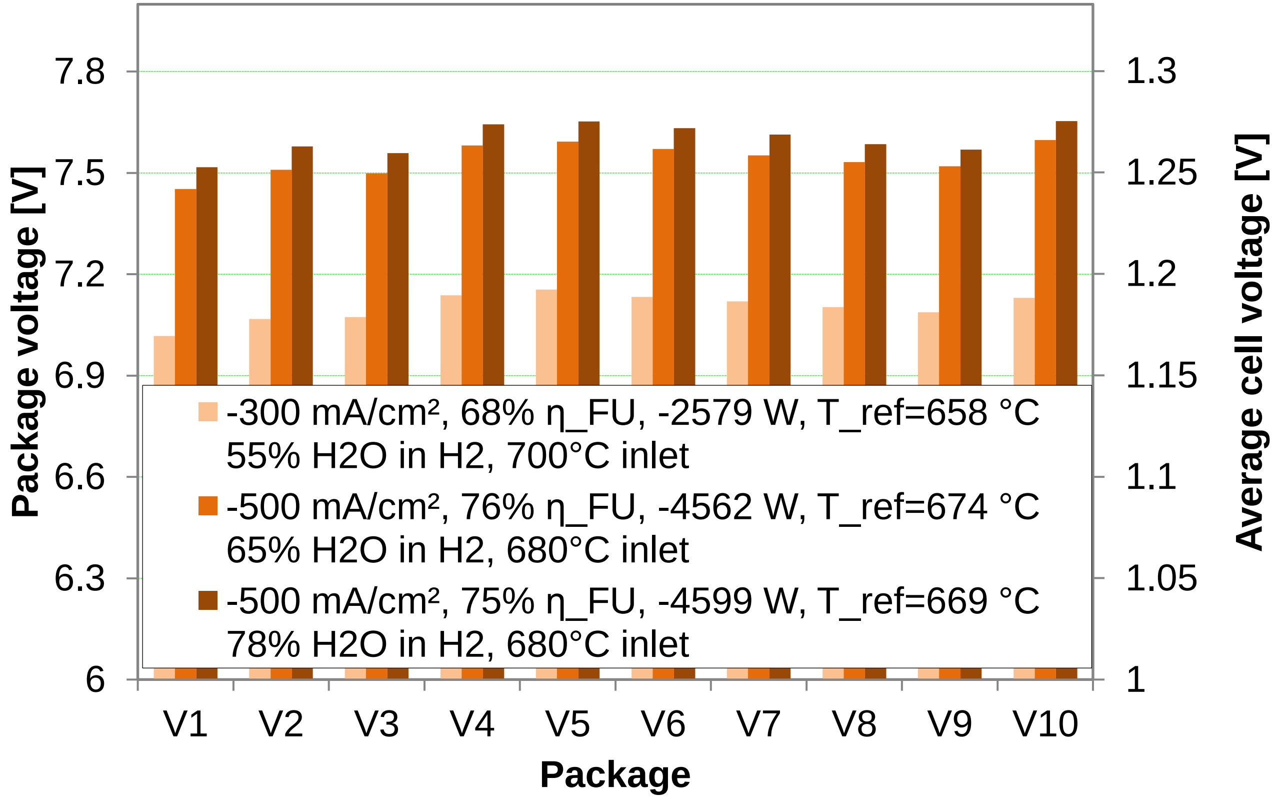
SOEC Elcogen protype

elcoStack E1500 module design, assembly and test

SOEC operation @ -500 mA/cm², SU 75 %, 80 % H_2O in H_2

- Power in reference point: P_{el}= -4.6 kW_{el}
- Stable and even voltage distribution

→ Successful result



4. Green hydrogen production

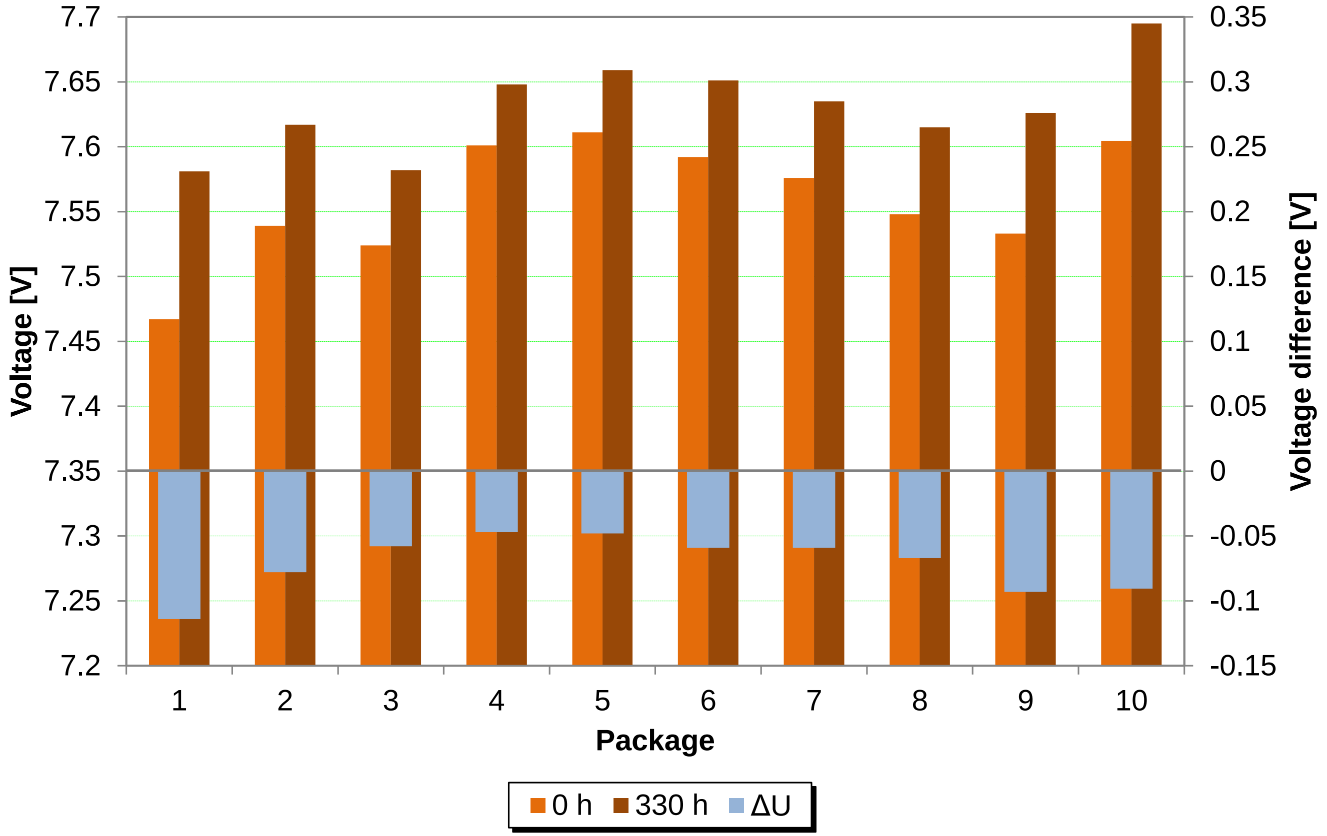
SOEC Elcogen protype

elcoStack E1500 module design, assembly and test

SOEC operation @ -500 mA/cm², SU 75 %, 80 % H_2O in H_2

- Long term test for 330 h with minor degradation of $\Delta P_{el} / P_{el}$ = 3 %/1000 h (@-500 mA/cm² 330 h)
- Stable operation possible

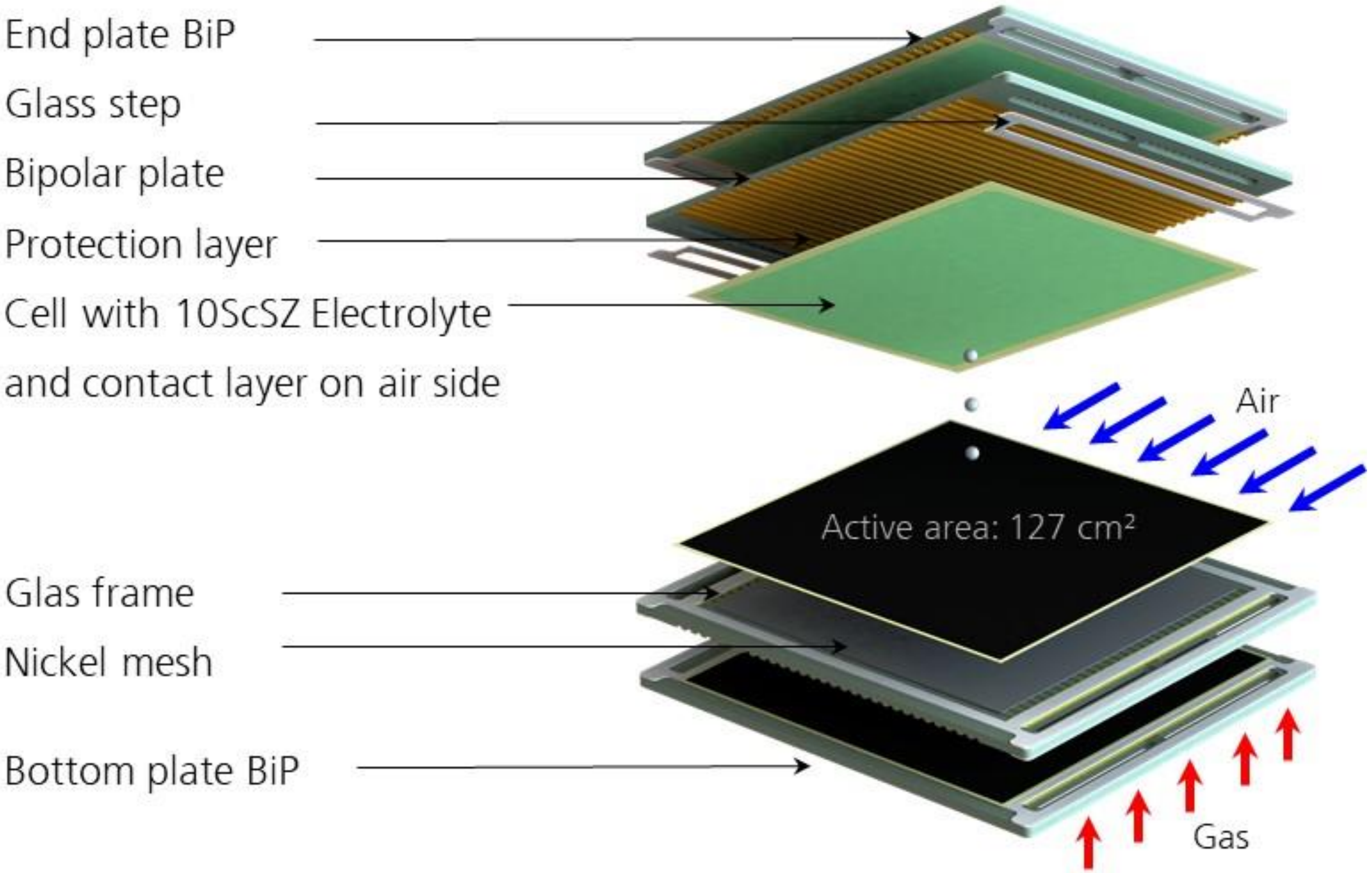
→ Good test



4. Green hydrogen production

SOEC development

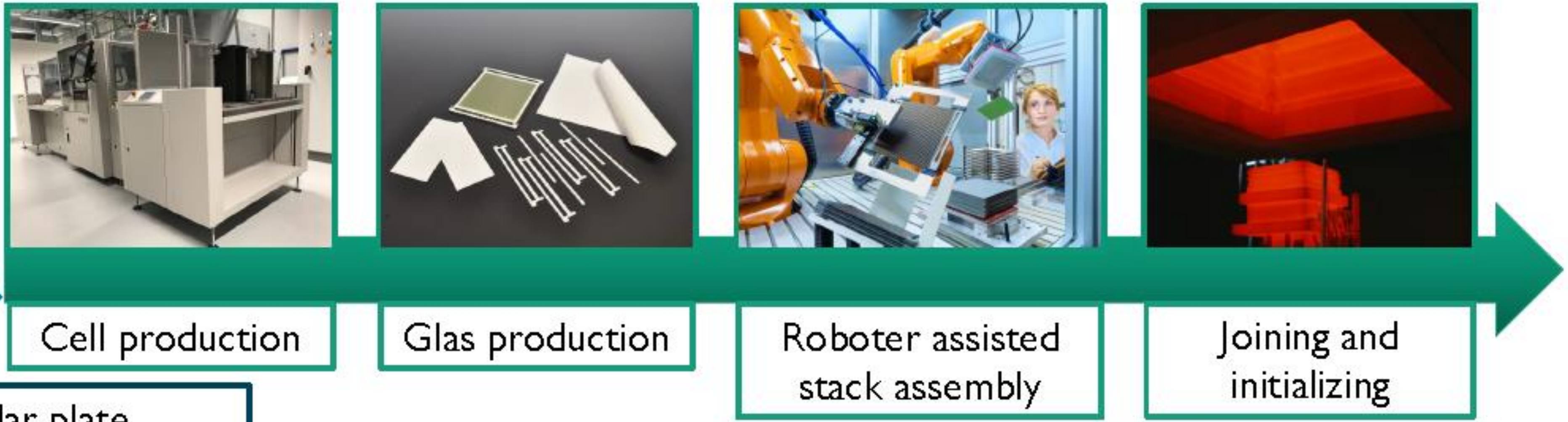
Development of modified electrolyte supported cells for SOEC (FhG-IKTS)



4. Green hydrogen production

SOEC development

Development of modified electrolyte supported cells for SOEC (FhG-IKTS)



Bipolar plate
Elektrolyte
Nickel mesh

- Continuous component inspection
- Stacks with 10-40 cells

SOEC development

Development of modified electrolyte supported cells for SOEC (FhG-IKTS)

- Decreasing the area specific resistance of the cell (ASR) by around 32%
  - Improving the electrodes:
    - Anode
    - Adhesion layer at the cathode
  - Decreasing the sintering temperature
  - Decreasing the substrate thickness

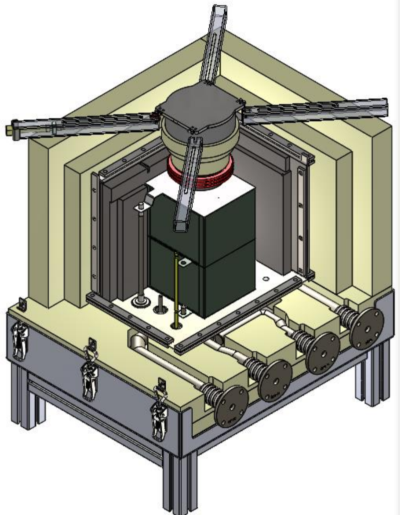
ASR (area specific resistance) of cell measured at 800 ° C, H2:H2O=1:1 without CCL

4. Green hydrogen production

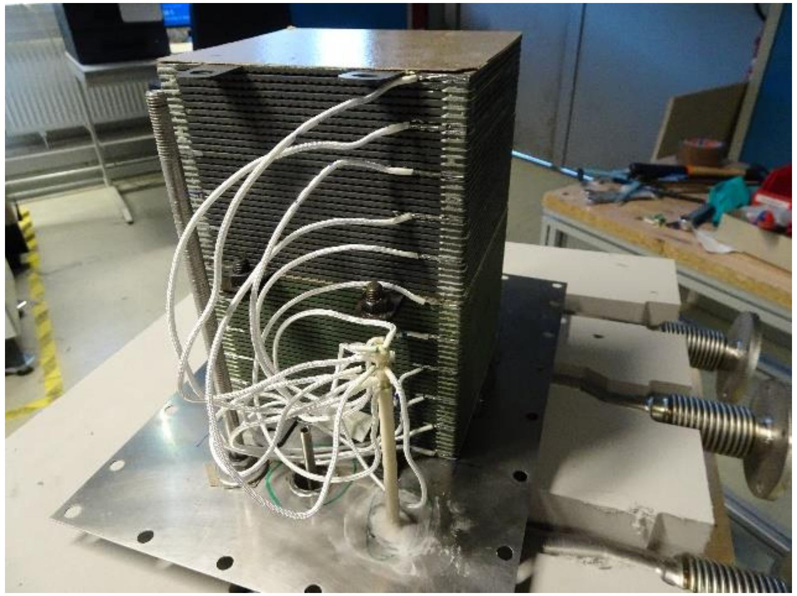
SOEC FhG-IKTS protype

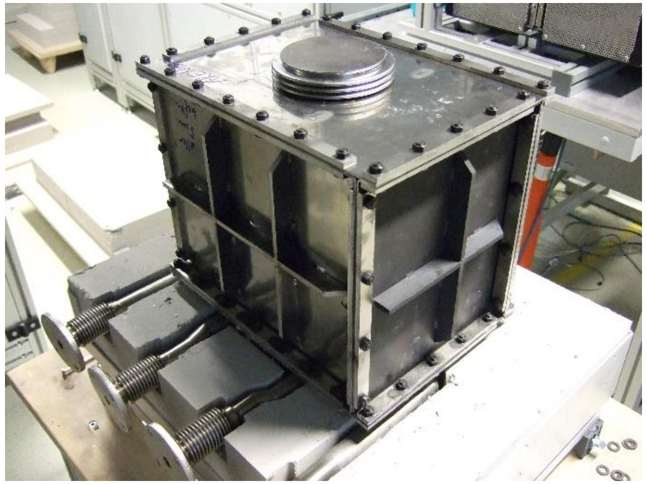
MK355 Stack module design, assembly and test

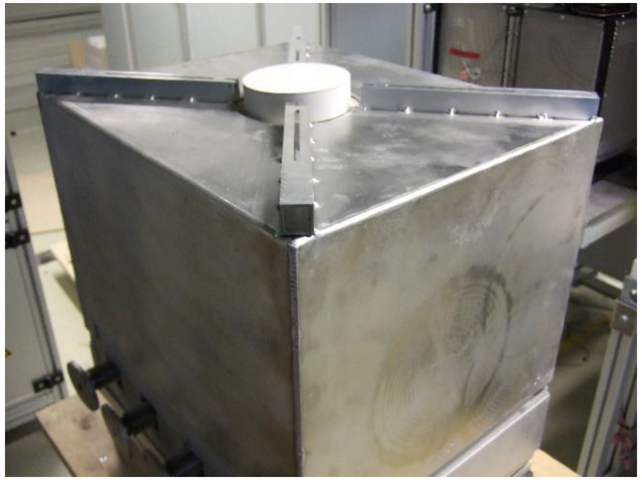
- Assembly of the 5-kW demo stack with IKTS stacks
- Assembly with no problems
- Test at test rig completed



CAD study of IKTS SOEC stack module







4. Green hydrogen production

SOEC FhG-IKTS protype

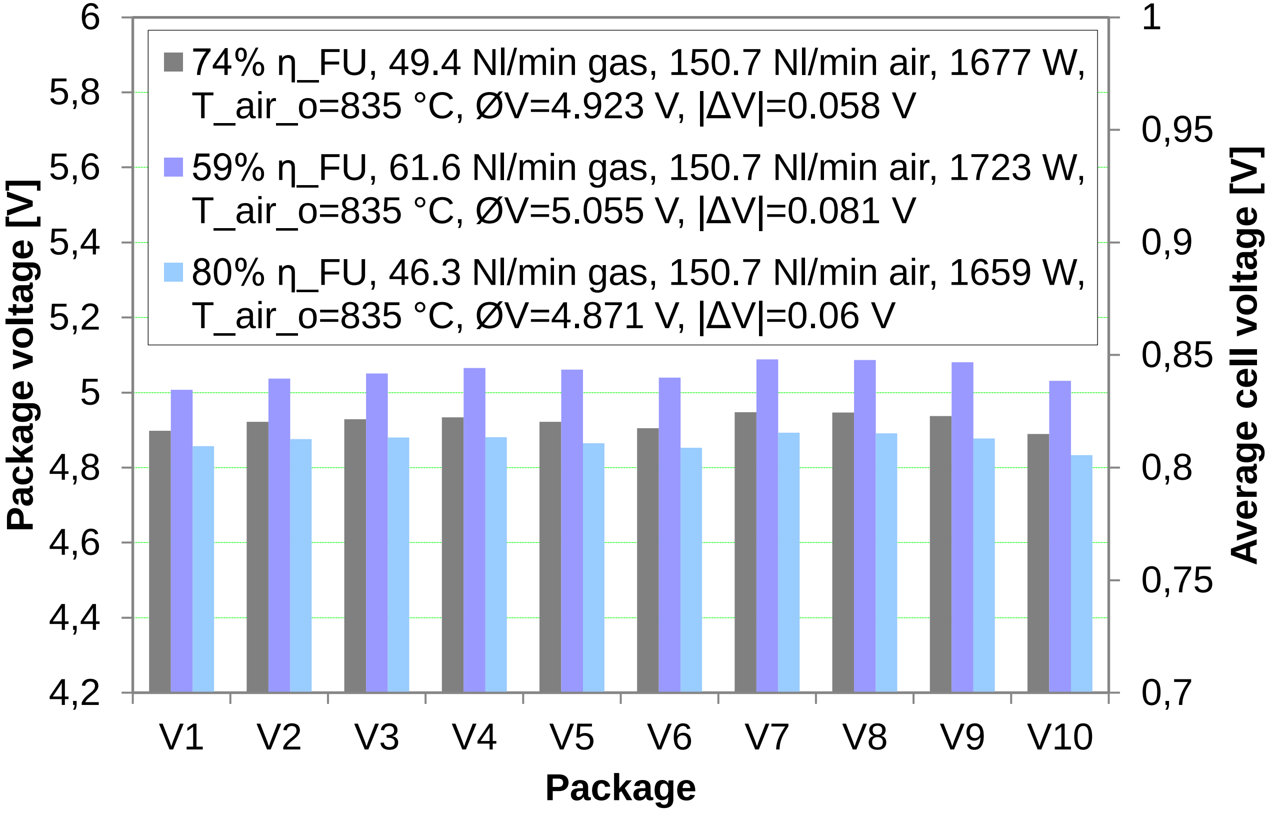
MK355 Stack module design, assembly and test

SOFC operation @35 A, T_{ref}=835°C, 40 %H_2 in N_2

- Power in reference point: P_{el}=1677 W_{el}
- Variation of fuel flow from 60% to 80%

  → Perfect result

  → Homogeneous gas supply



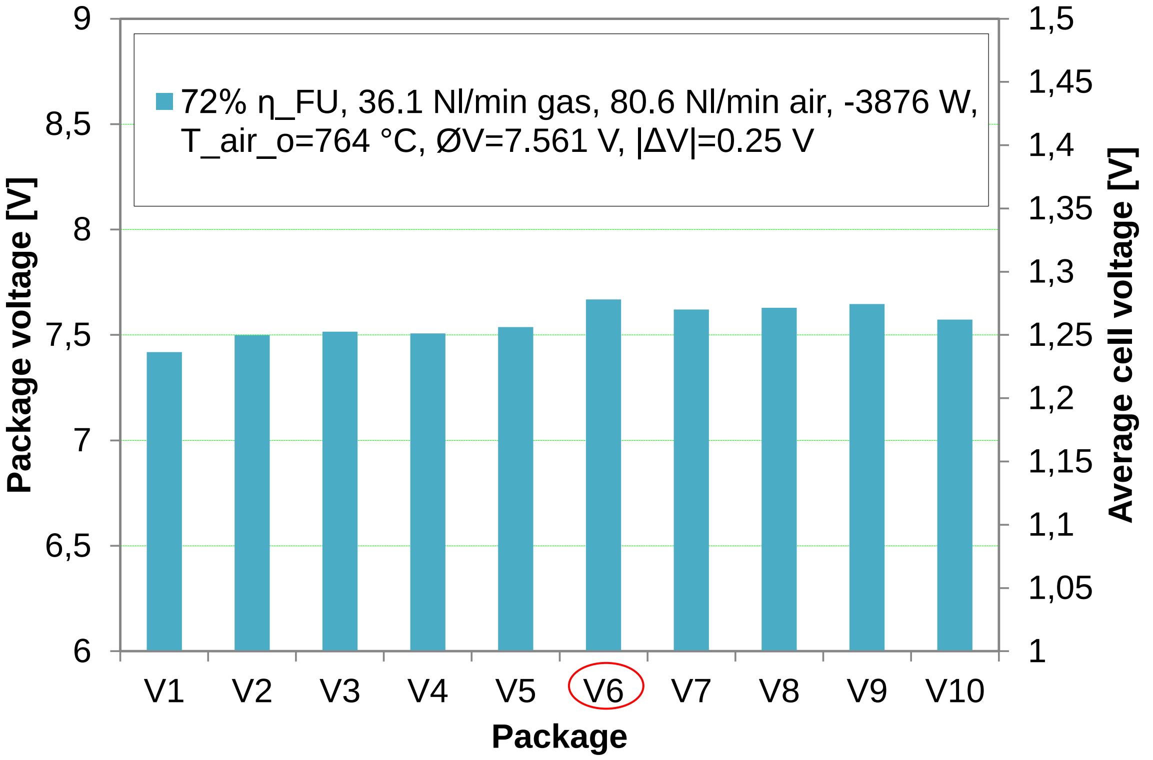
SOEC FhG-IKTS protype

MK355 Stack module design, assembly and test

SOEC operation in Co-electrolysis mode @-50 A (part load)

- Gas composition: 10% H_2, 56 % H_2O, 10 % CO, 24% CO_2
- H/C=2 with 20 % reducing gas

→ Comparable values for steam electrolysis (i.e.: 80%H_2O in 20 % H_2)



Voltage measurement includes current plug

→ SOEC prediction with 120 W/cell >7 kW possible

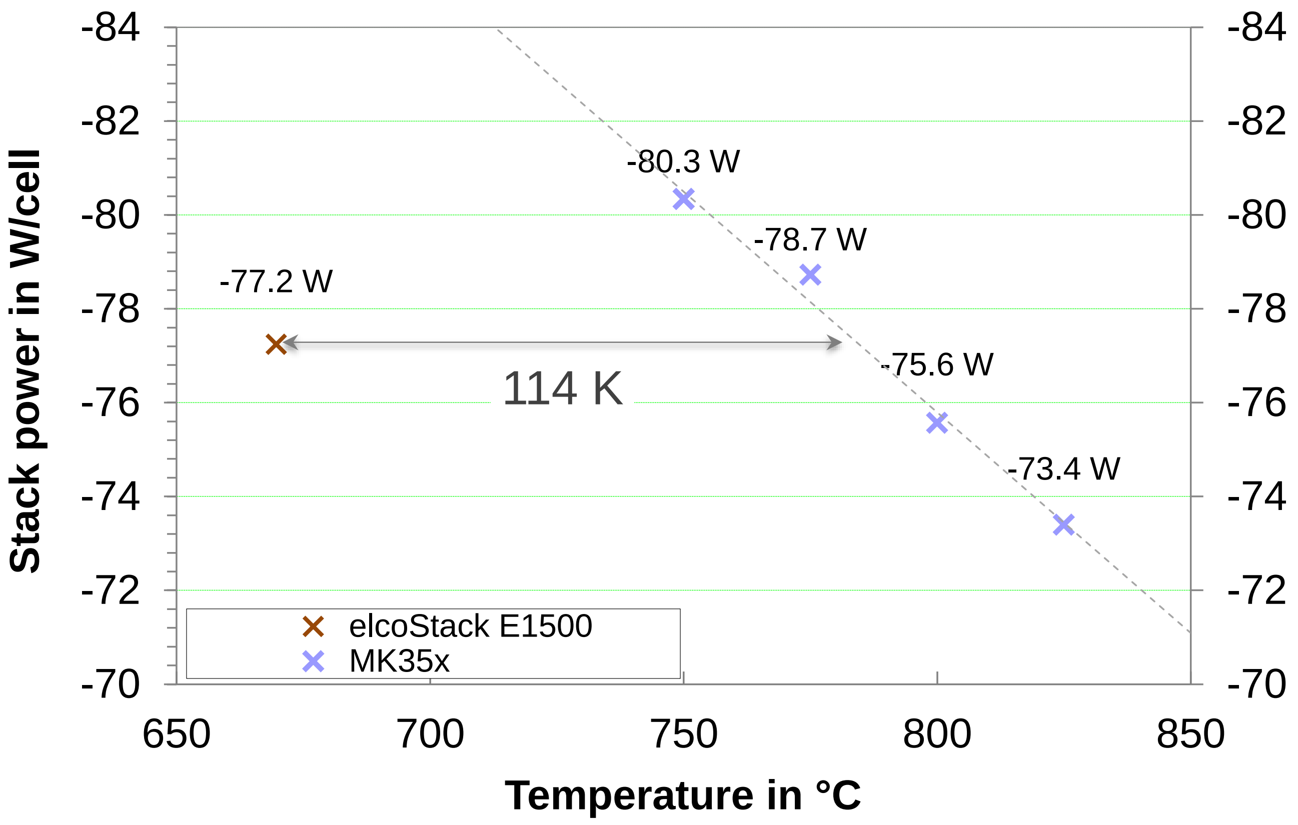
→ More than 25 Nl/min H_2 from MK355 SOEC prototype

4. Green hydrogen production

Comparison of elcoStack E1500 to MK35x

SOEC operation @ -500 mA/cm², SU 75 %, 80 % H_2O in H_2

- Power of elcoStack E1500 comparable
  MK35x stack 60 cell with temperature difference 114 K
- ElcoStack E1500 operated at maximum temperature whereas MK355 has wide operation window



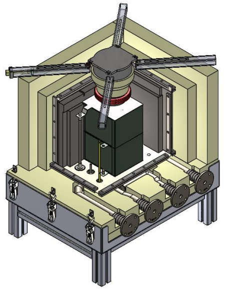
4. Green hydrogen production

SOEC development

Conclusion

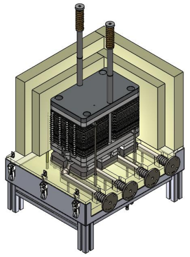
Fraunhofer IKTS

- Stack tests with new cells: increased max. current density to -700 mA/cm²
- Up to -120 W/cell can be converted to H_2
- -115 W/cell @Tref=800° C, -700 mA/cm², hFU=75%
- Wide temperature window 750-860° C (Fuel: 80% H_2O in 20% H_2, Air: 30 Nl/min)
- 2x30-cell MK35x stack module commissioned for 25 Nl/min H_2 production at CNH2 for Haber Bosch



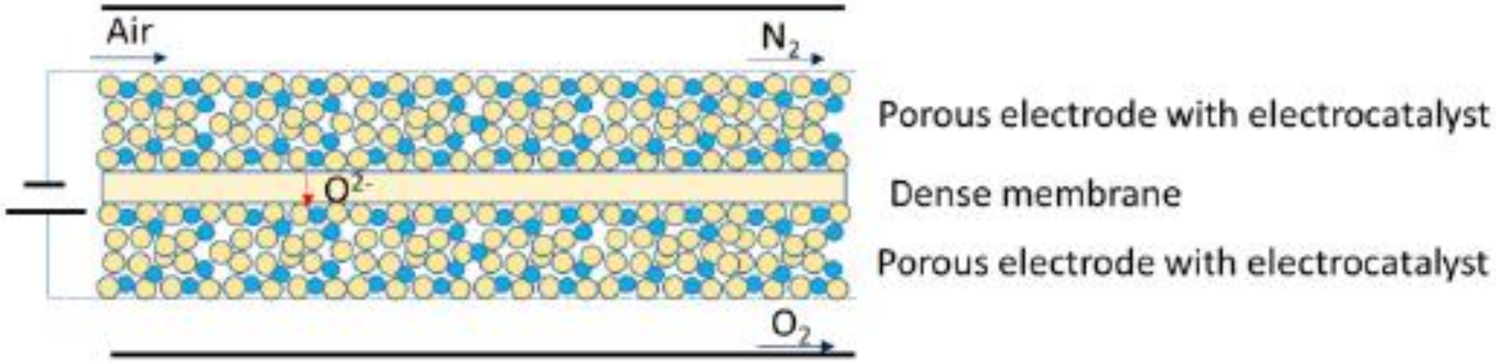
elcogen
Affordable green hydrogen

- Single cell tests with experimental electrodes: Addition of iron to hydrogen electrode increased performance
- Short stack test with multiple experimental cells showed that the addition of iron also decreased stabilization time in the stack.
- E1500 stack module assembled and commissioned at IKTS
- Constant operation at -500 mA/cm² at IKTS

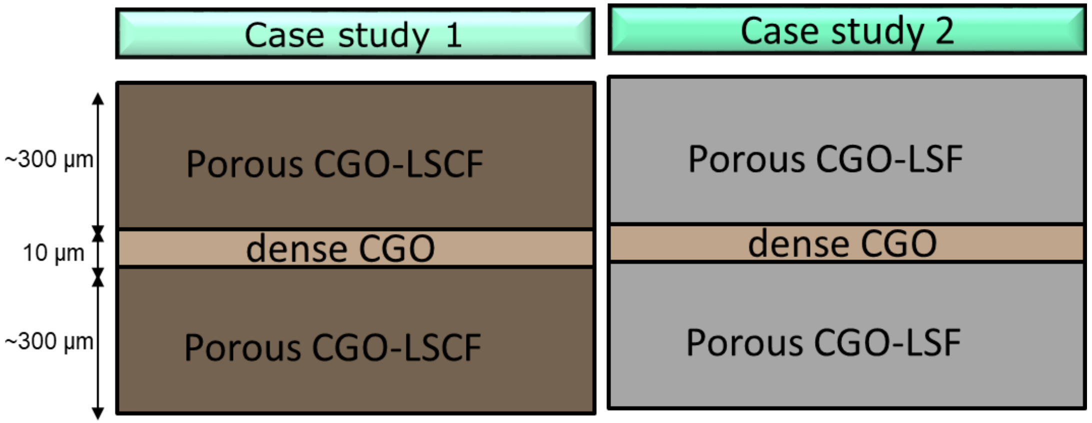


5. Green nitrogen production

The concept – electrochemically split Air to N_2 and O_2:



Two types of electrochemical cells backbone been developed



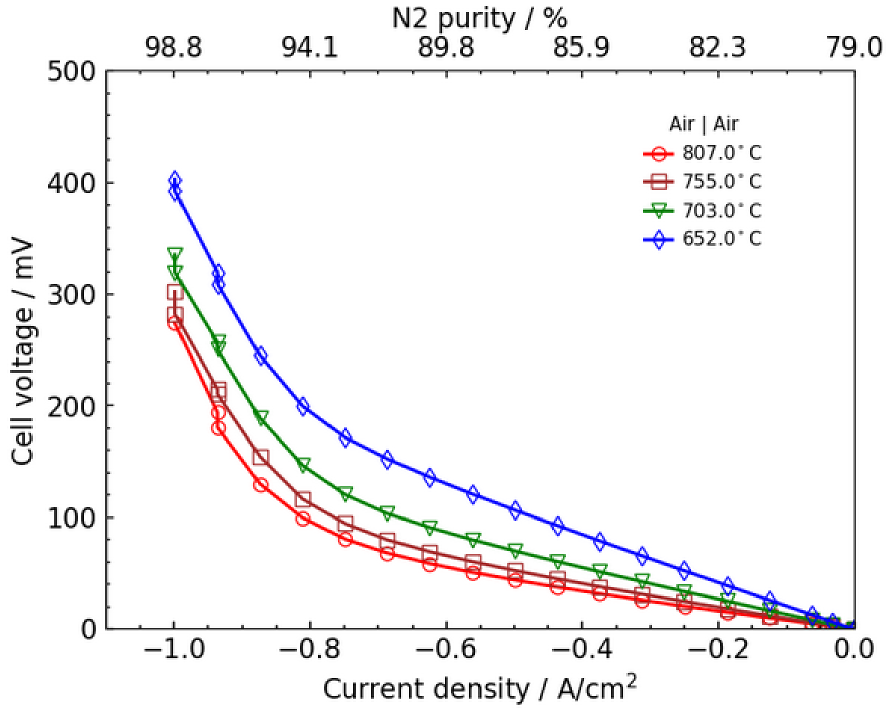
CGO = $Ce_{0.9}Gd_{0.1}O_{1.95}$

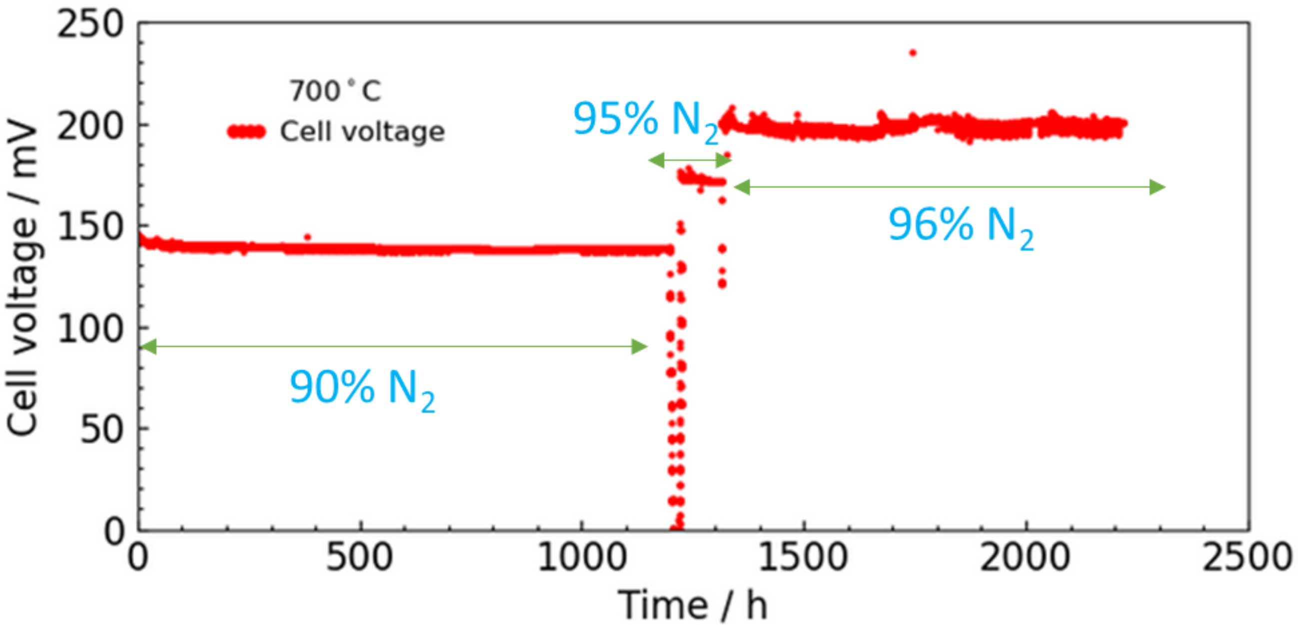
LSCF = $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

LSF = $La_{0.6}Sr_{0.4}FeO_{3-\delta}$

5. Green nitrogen production

Performance and durability of Case study 1 cell infiltrated with catalyst

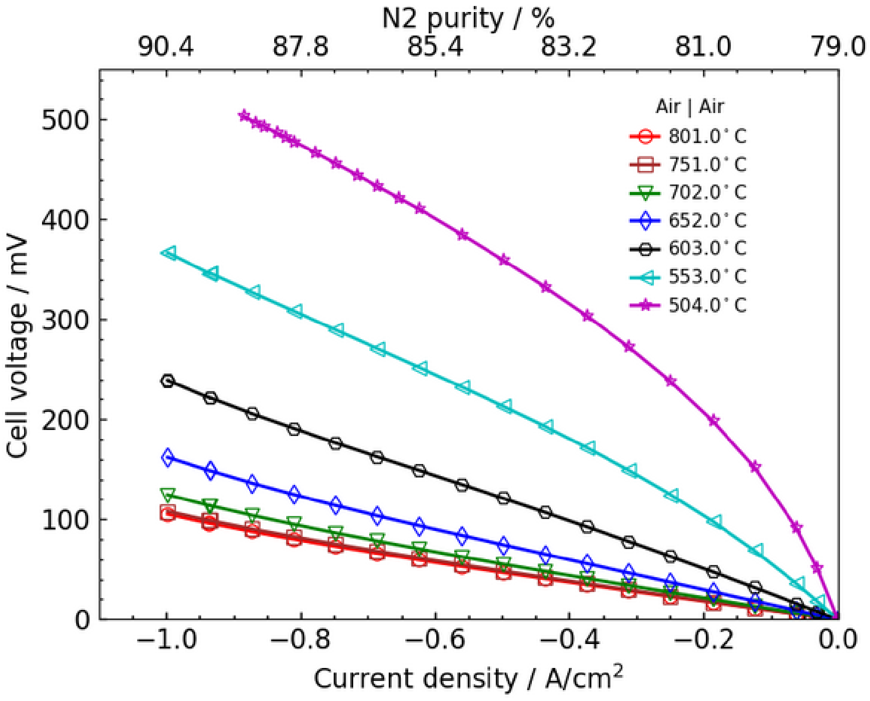


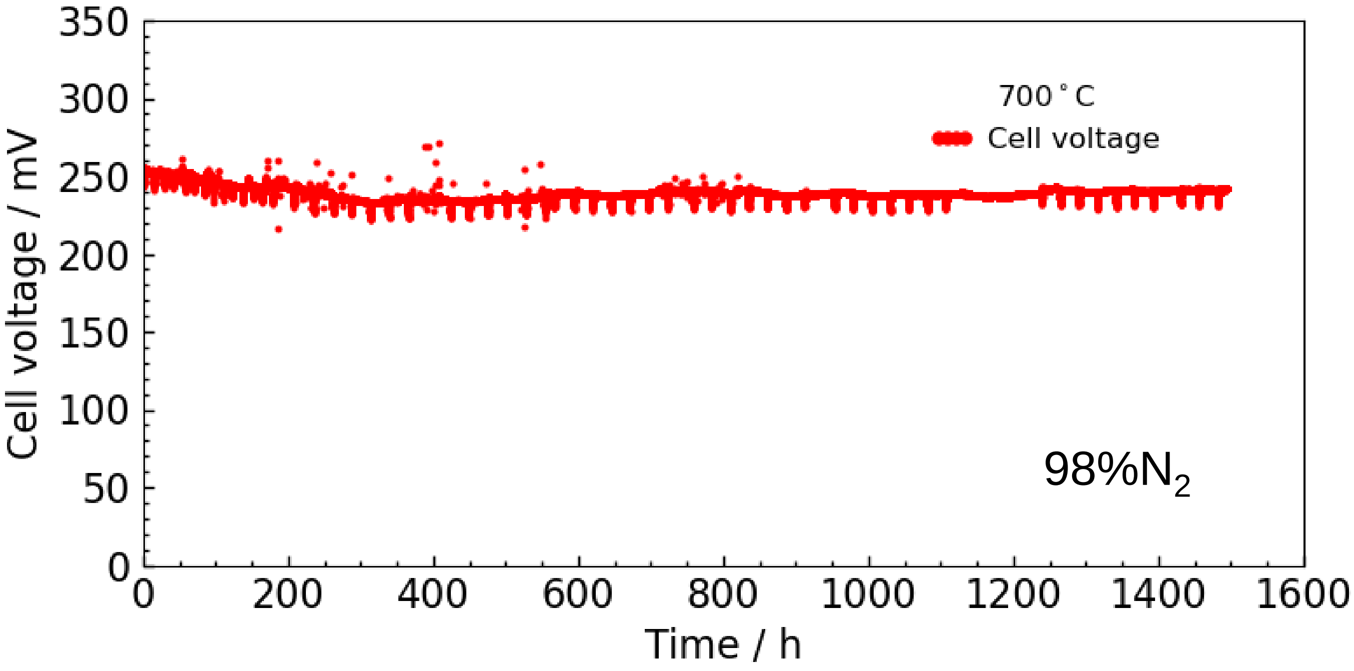


- Low overpotential at 650-800 °C and current density below 0.8A/cm^2
- Durable for high purity N_2 production

5. Green nitrogen production

Performance and durability of Case study 2 cell infiltrated with catalyst

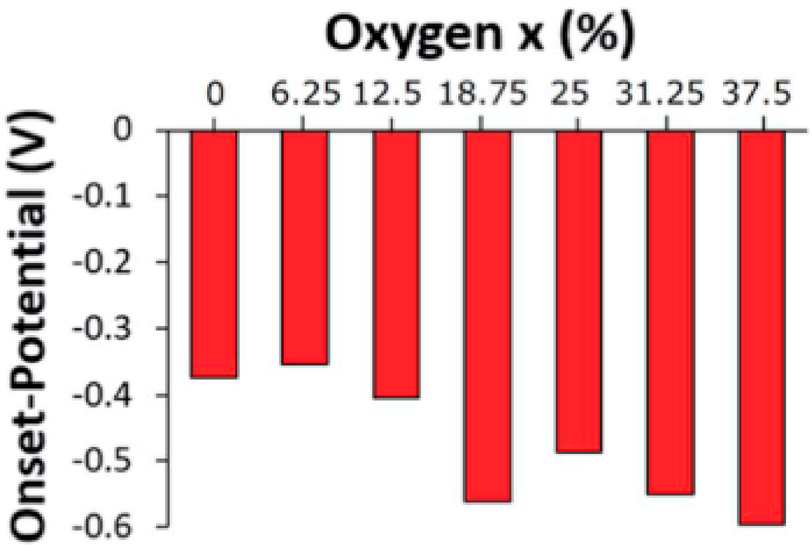




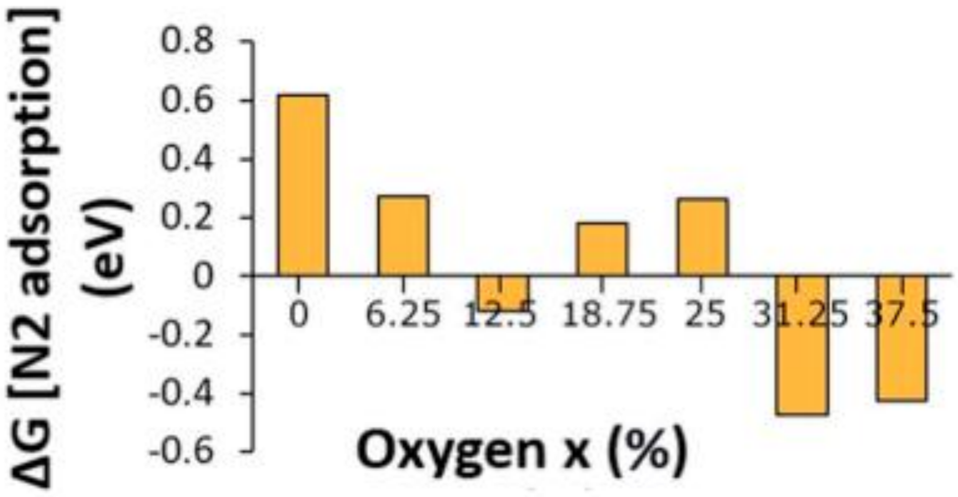
- Low over potential over a wild operation temperature range
- Durable for high purity N_2 production

6. Green ammonia production

DFT study performed on VNOx for potential catalyst for NH_3 electrosynthesis



Theoretical onset potential decrease with O concentration (overpotential increase)



The thermodynamic barrier to N_2 adsorption decrease with O concentration

- Transition metal nitrides are active for the N_2 reduction to NH_3 but deactivates over time.
- Active sites are thought to be close to surface O.

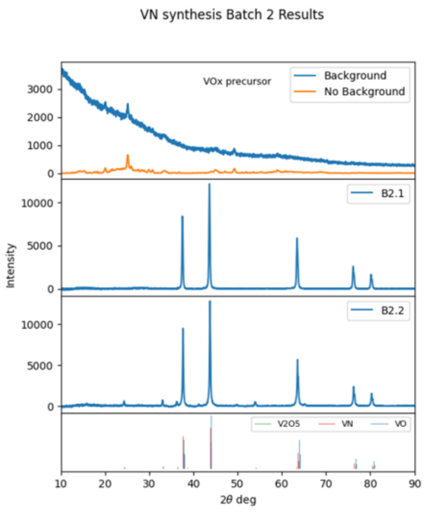
6. Green ammonia production

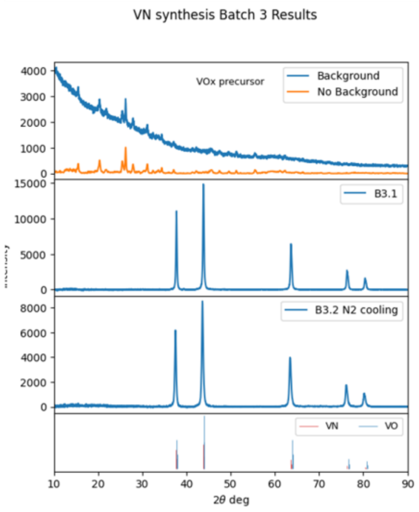
Synthesis of VNOx materials

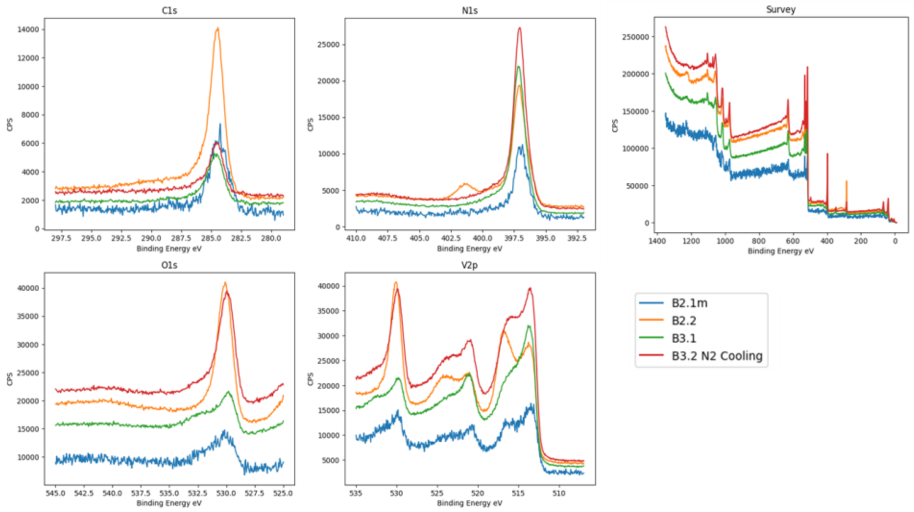
VNOx synthesized and studied with XRD, XPS to confirm the phase and surface status

$2NH_4VO_3 + 2CO(NH_2)_2 \rightarrow 2VO_2 + 2CO_2 + 4H_2O + 3N_2$

$2NH_3 + 2VO_2 \rightarrow 2VNO + 3H_2O$

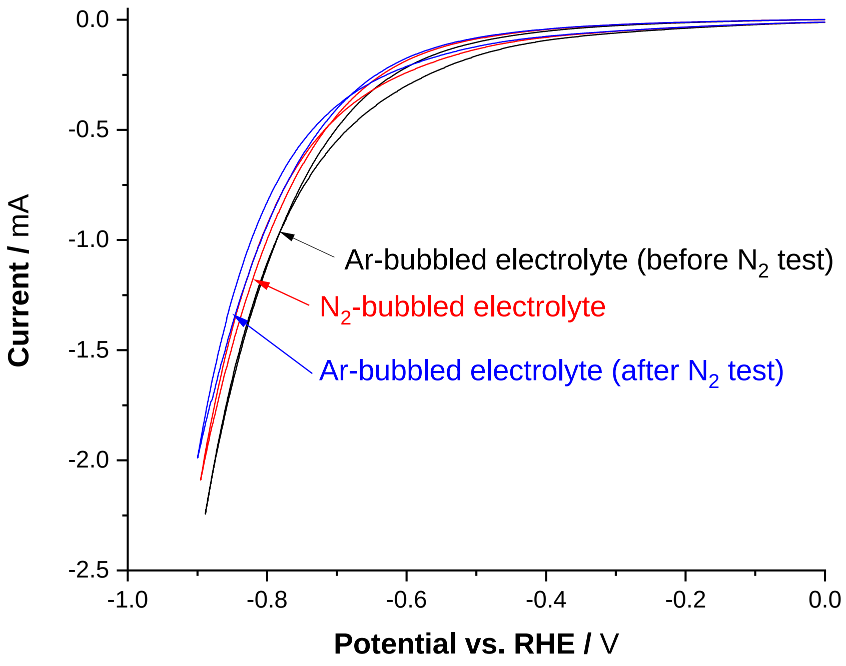


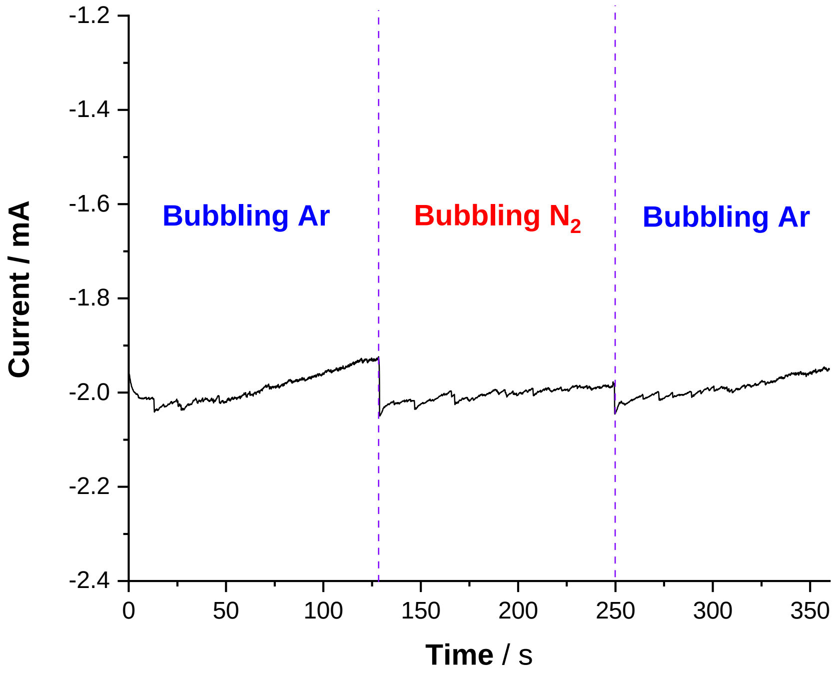




6. Green ammonia production

Electrochemical characterization with Rotating disc electrode experiment



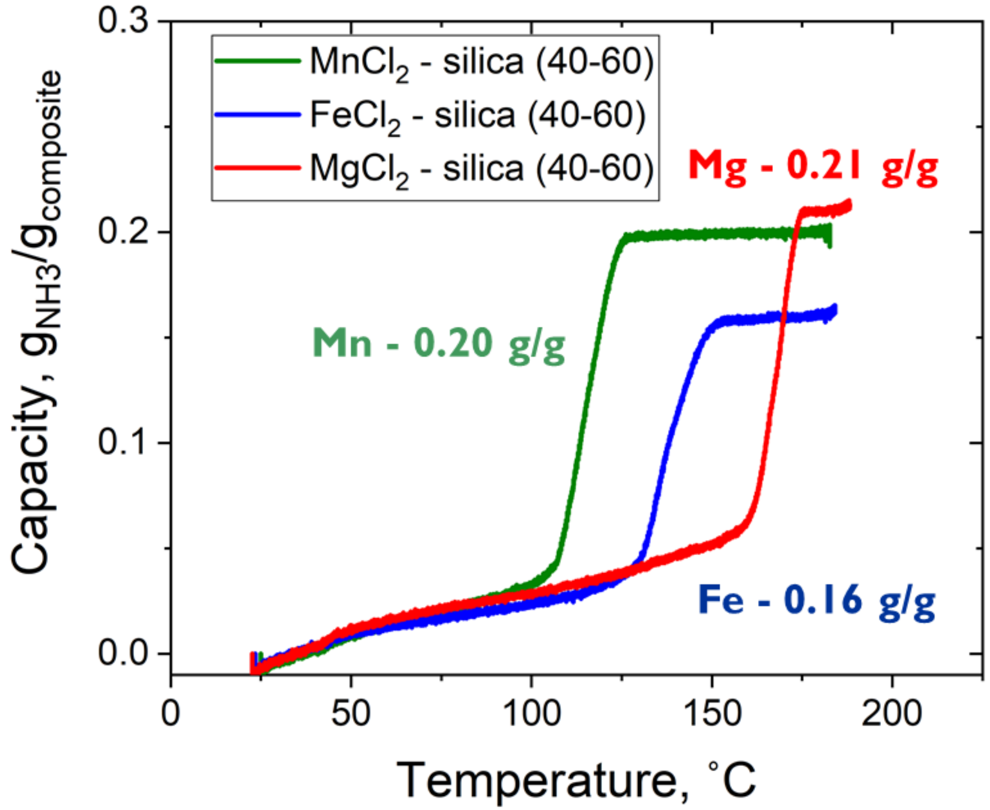


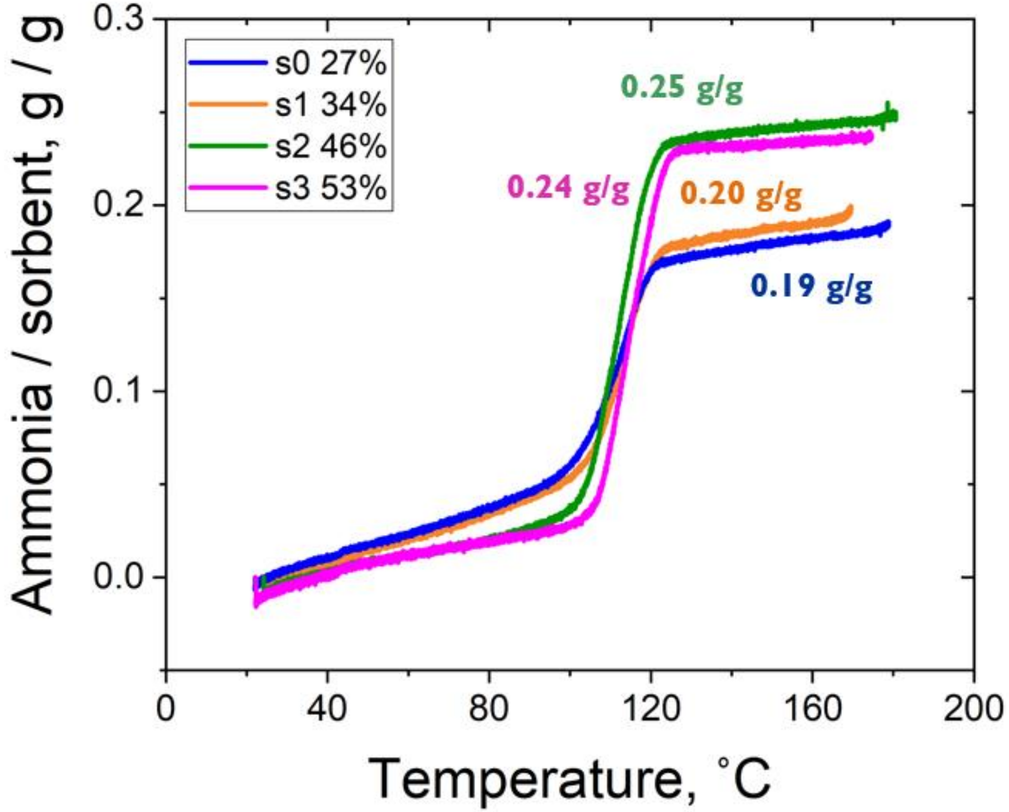
Electrolyte solution: 0.1M $HClO_4$, 1600RPM, catalyst load 68 μg/cm$^2_{GC}$

- No electroactivities observed for NH_3 synthesis, H_2 evolution dominate the reaction

7. Advance ammonia synthesis loop: sorbent

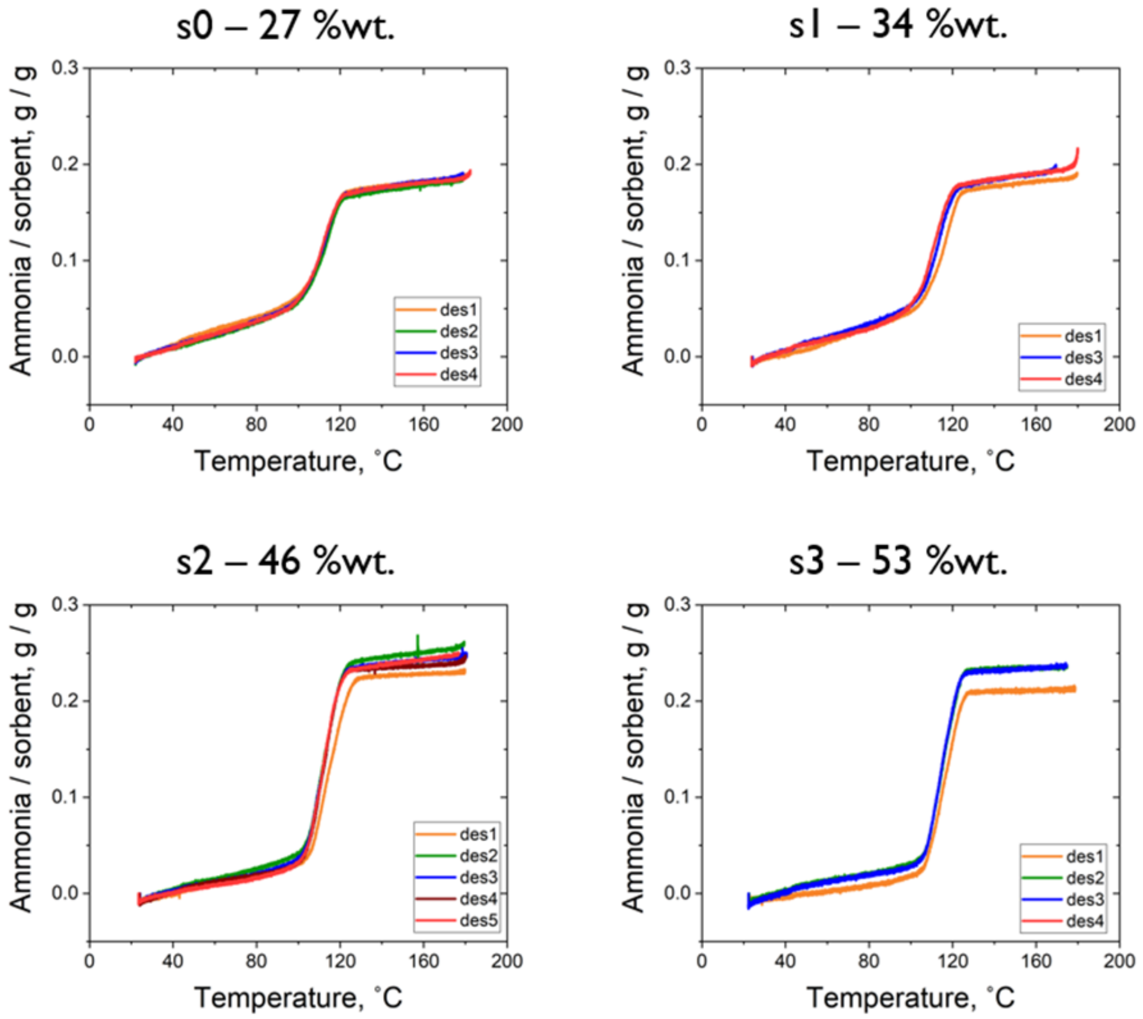
Absorbent material selection and capacity optimization





7. Advance ammonia synthesis loop: sorbent

Absorbent material stability upon sorption/desorption cycles

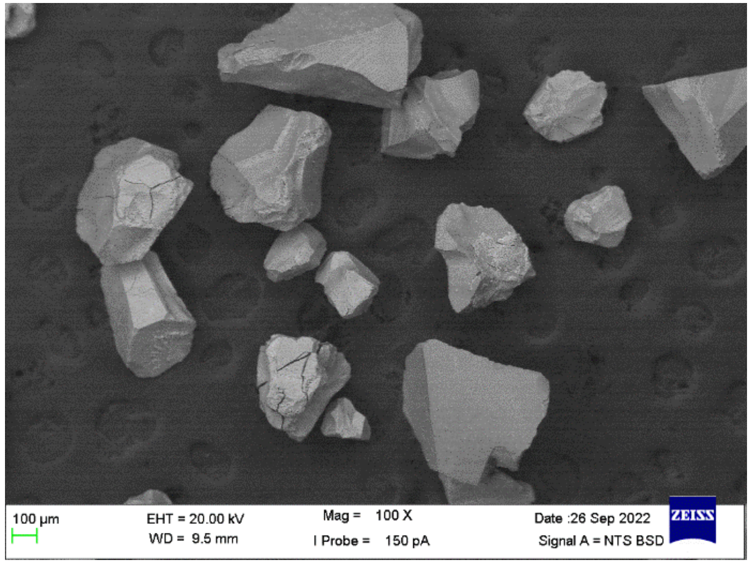


7. Advance ammonia synthesis loop: sorbent

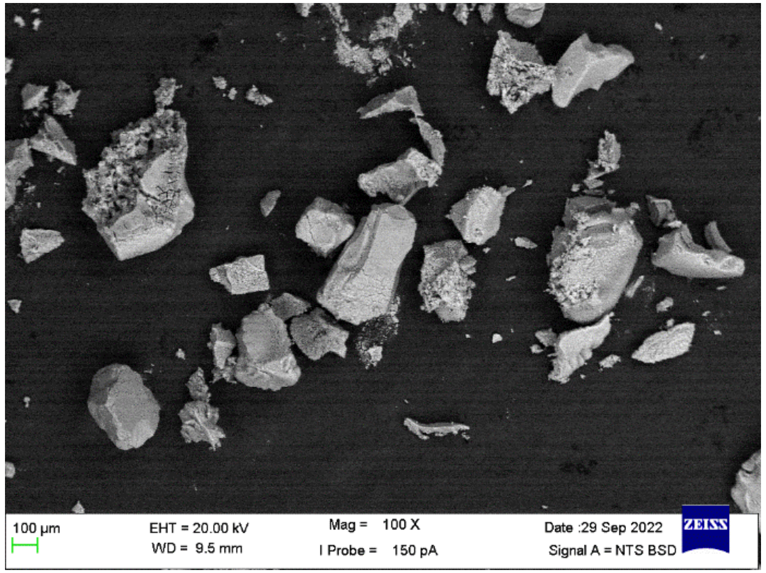
Absorbent material stability upon sorption/desorption cycles

Sg + $MnCl_2$ (**34**%wt.)

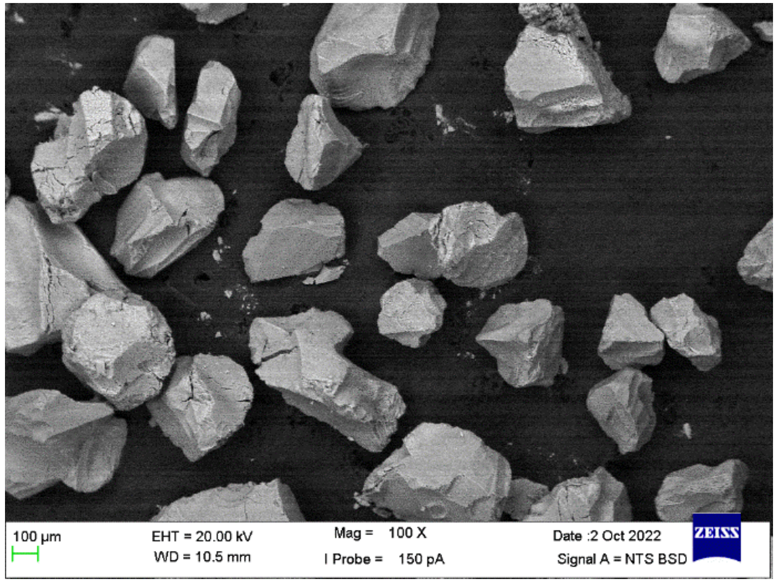
Before cycling



After full cycling



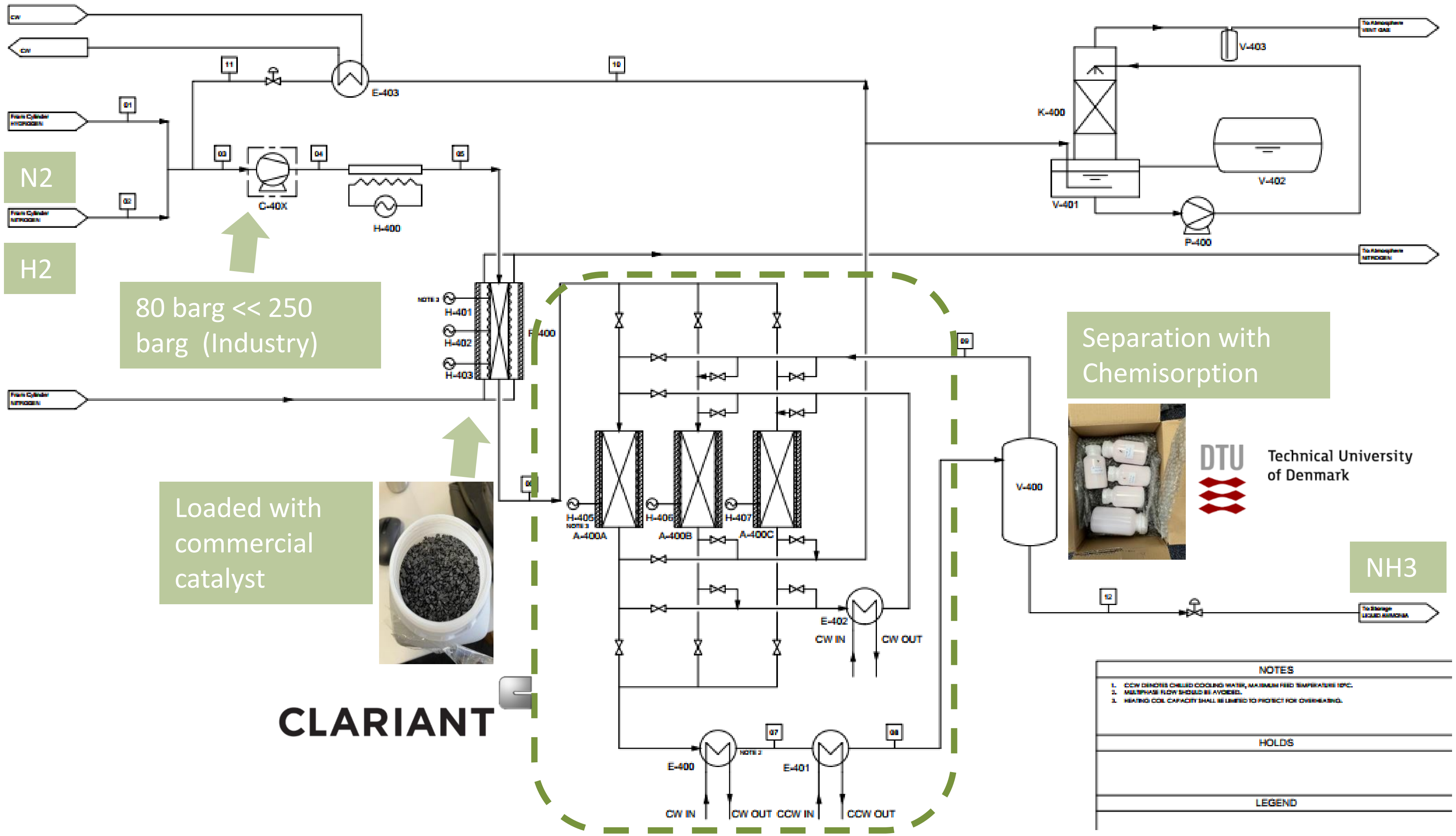
After partial cycling



Full cycling: $MnCl_2 \rightarrow Mn(NH_3)_6Cl_2 \rightarrow MnCl_2 \ldots$

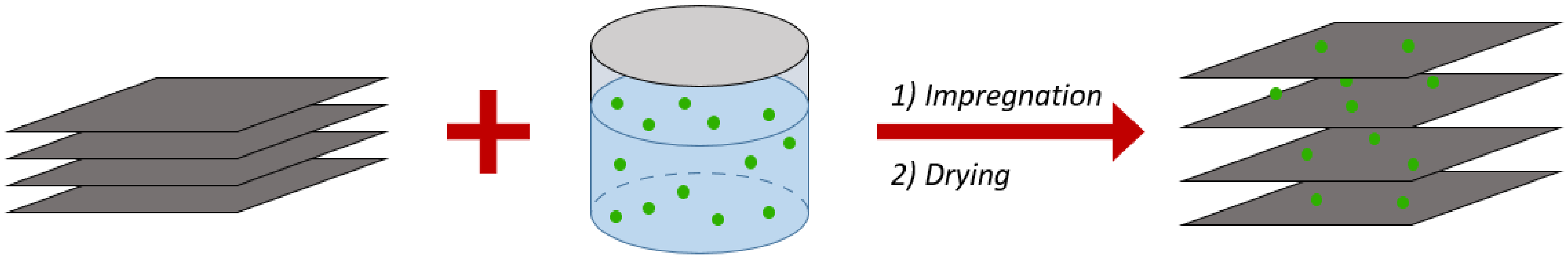
Partial cycling: $MnCl_2 \rightarrow Mn(NH_3)_6Cl_2 \rightarrow Mn(NH_3)_2Cl_2 \rightarrow Mn(NH_3)_6Cl_2 \ldots$

7. Advance ammonia synthesis loop: prototype



7. Advance ammonia synthesis loop: prototype

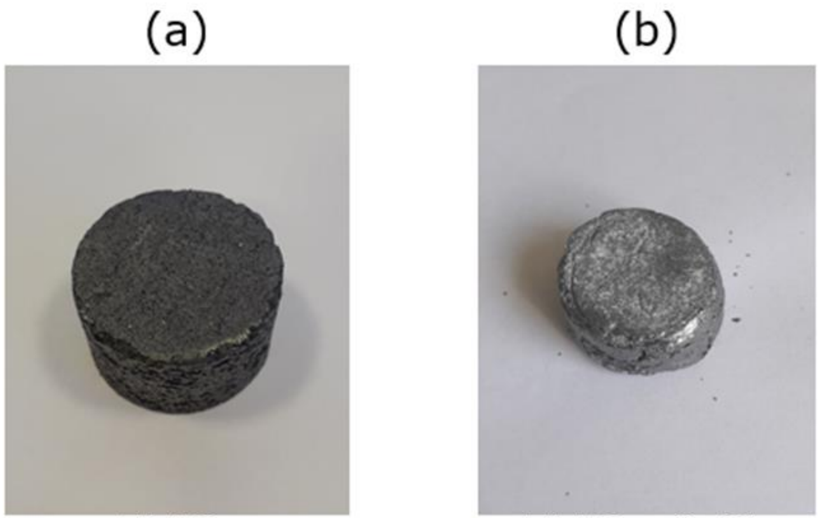
8. Solid state ammonia storage



Sigratherm ENG Board

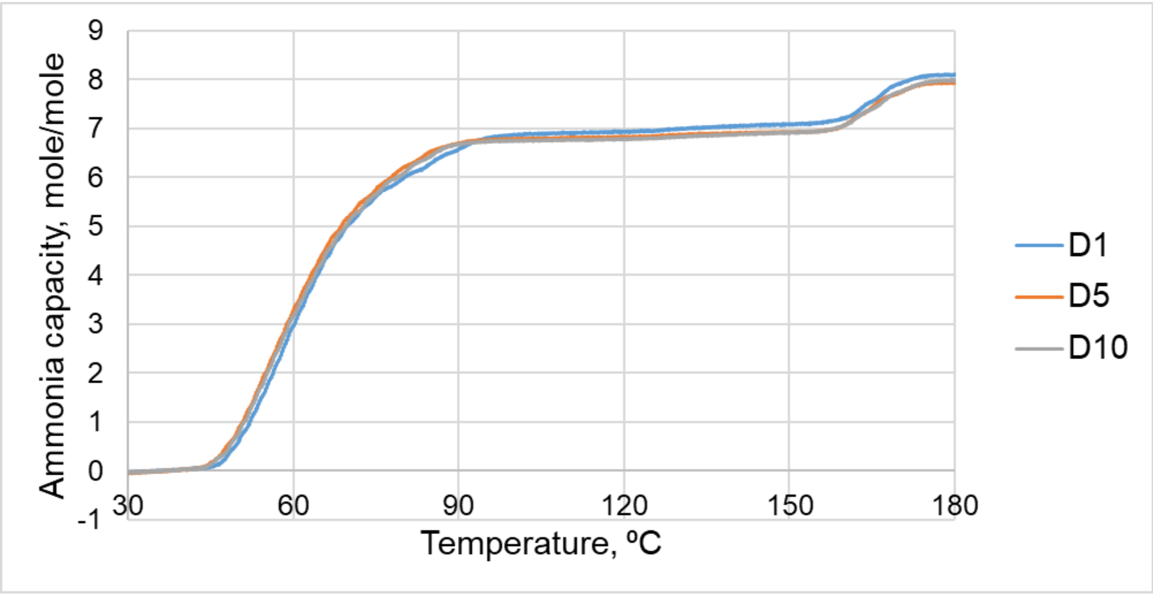
Aqueous $SrCl_2$ solution

ENG - $SrCl_2$ composite



ENG

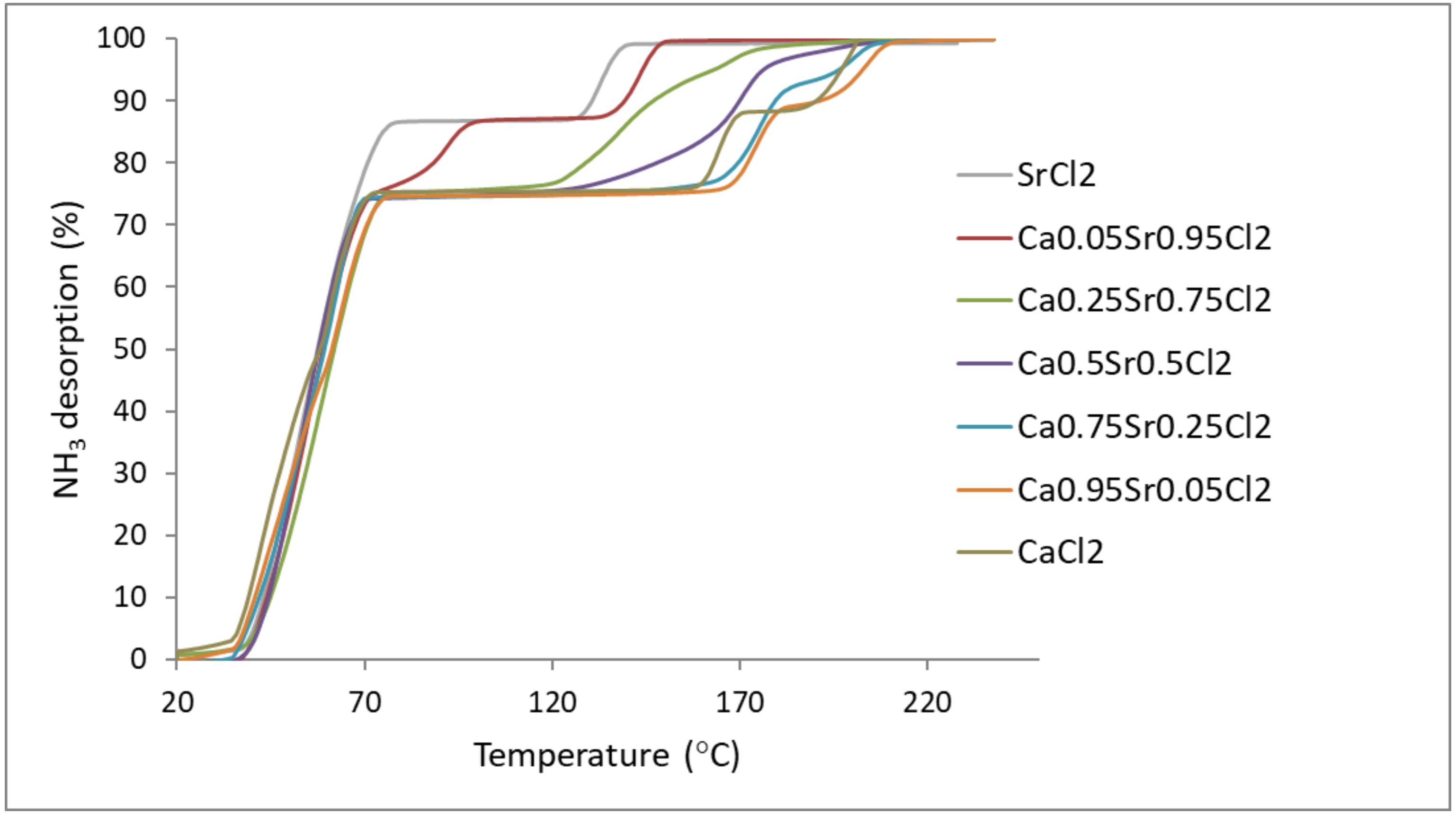
ENG – $SrCl_2$



8. Solid state ammonia storage

Sr-Ca chloride mixtures

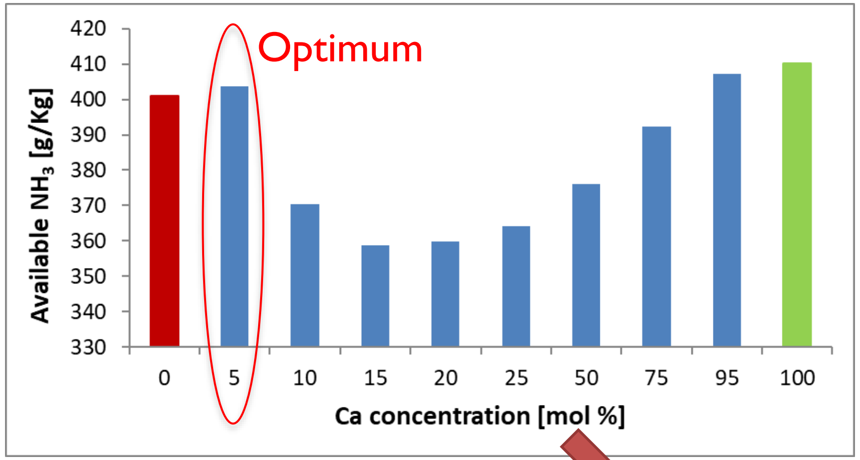
Desorption curves of Sr-Ca chloride mixtures obtained at 1 bar of NH_3 pressure on TGA



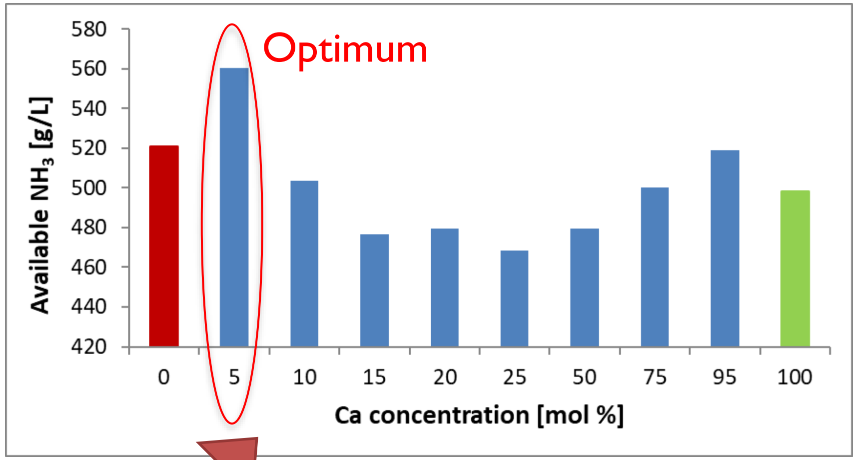
8. Solid state ammonia storage

Optimize with cheaper materials -- Sr-Ca chloride mixtures

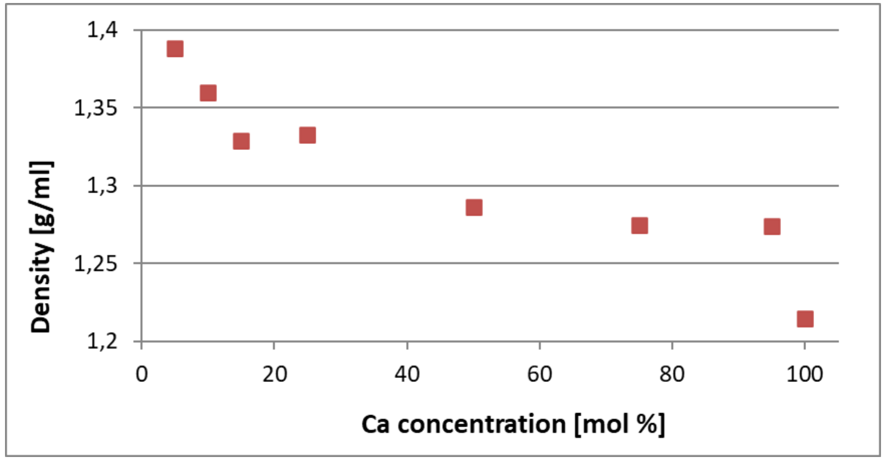
Gravimetric capacity



Volumetric density

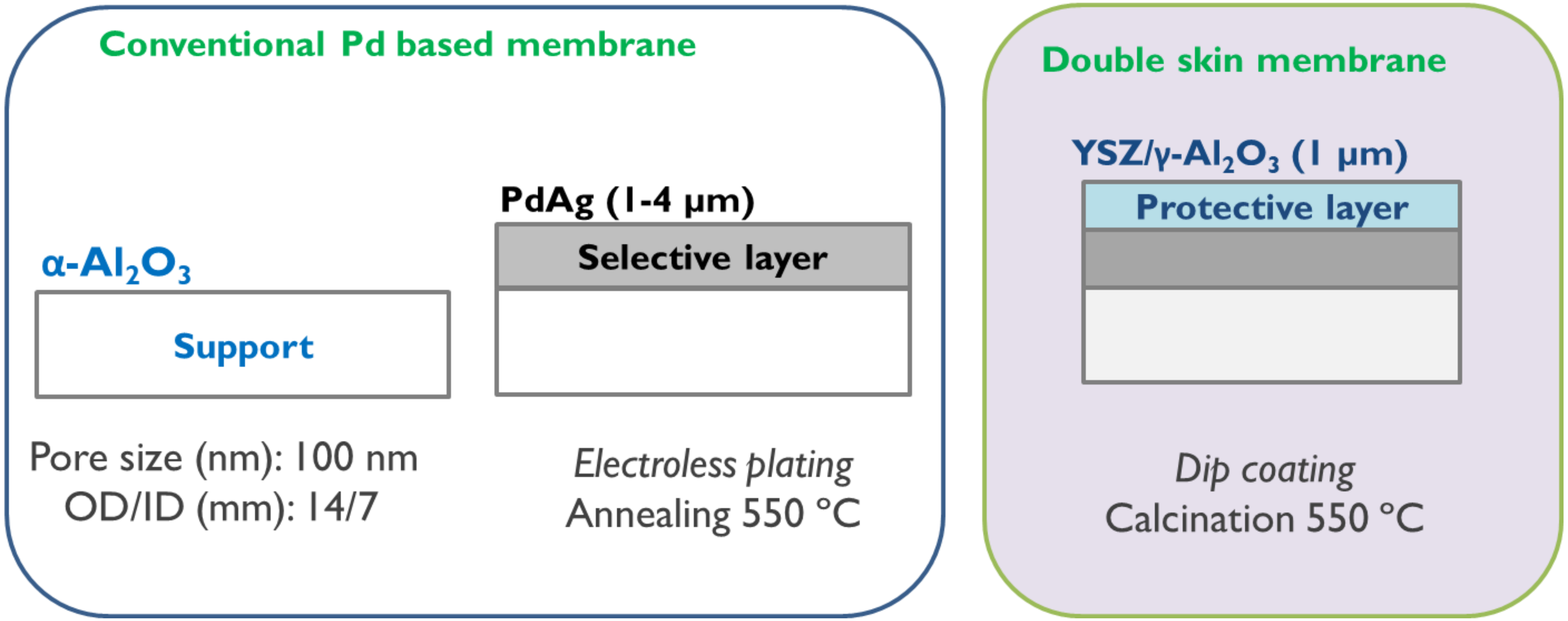


Tapped density



9. Ammonia decomposition

Development of double skin (DS) Pd based membranes for hydrogen separation membranes for ammonia decomposition reaction



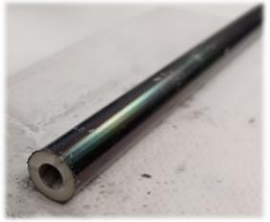
Goal: High H_2 permeance and H_2/N_2 & H_2/NH_3 selectivity

Target: Low N_2 permeance/leakage at RT

- 1st generation membranes: **< $2 \cdot 10^{-10}$ mol m^{-2} s^{-1} Pa^{-1}** **Achieved**
- 2nd generation membranes: **< $4 \cdot 10^{-11}$ mol m^{-2} s^{-1} Pa^{-1}** **Achieved**

9. Ammonia decomposition

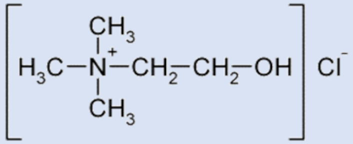
Recycling of Pd-based membranes



Evaluation of different DES leaching medias

Hydrogen bond acceptor

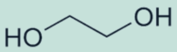
Choline Chloride



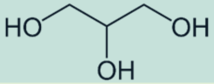
Hydrogen bond donors

Alcohols

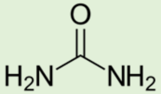
Ethylene glycol



Glycerol

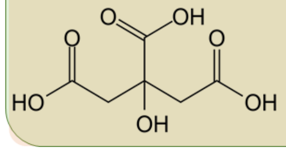


Urea

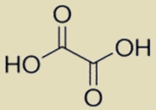


Acids

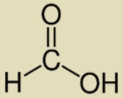
Citric acid



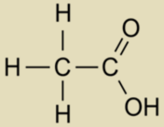
Oxalic acid



Formic acid

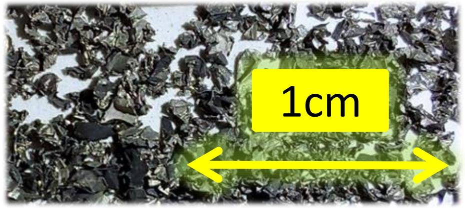


Acetic acid

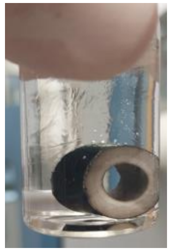


+ additives

Acid	HCl	Chloride	NaCl	Oxidizing agent	H_2O_2



>90% Pd & Ag leaching (grinded residue)



Similar recovery yield for full spent membrane

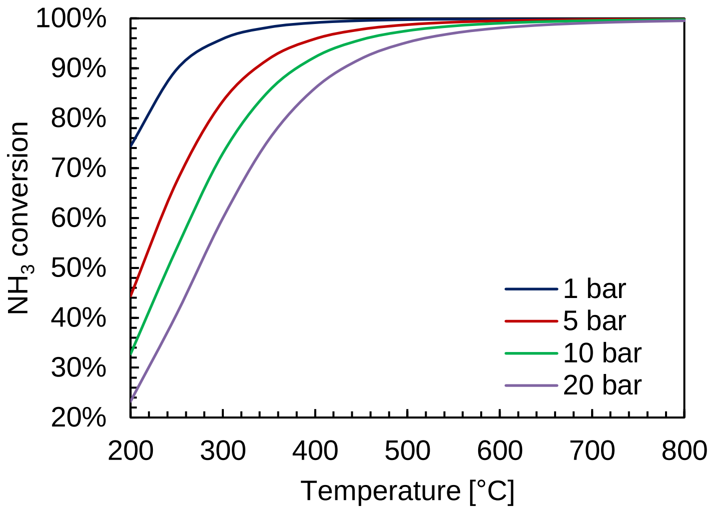
9. Ammonia decomposition

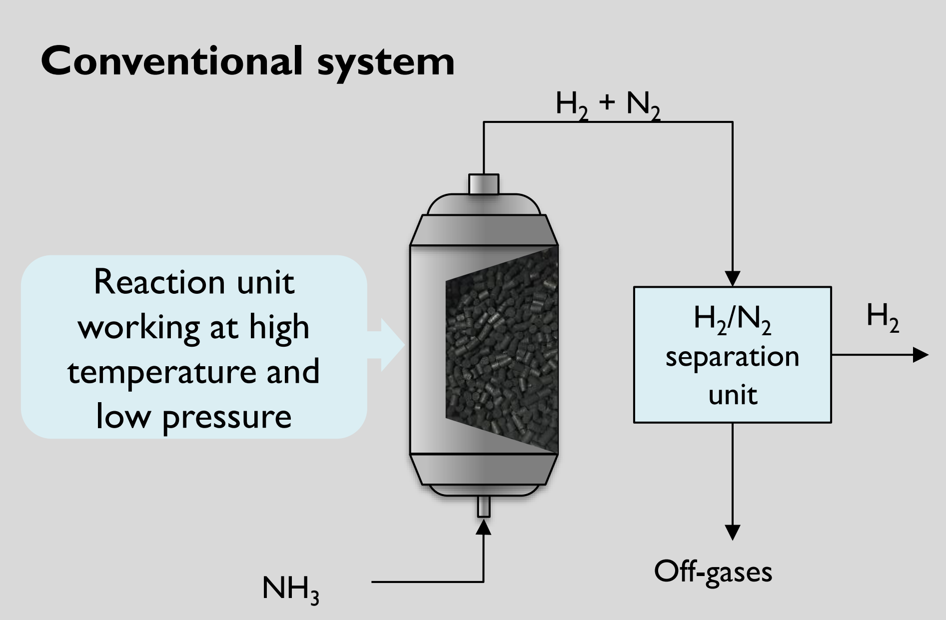
H_2 production via NH_3 decomposition

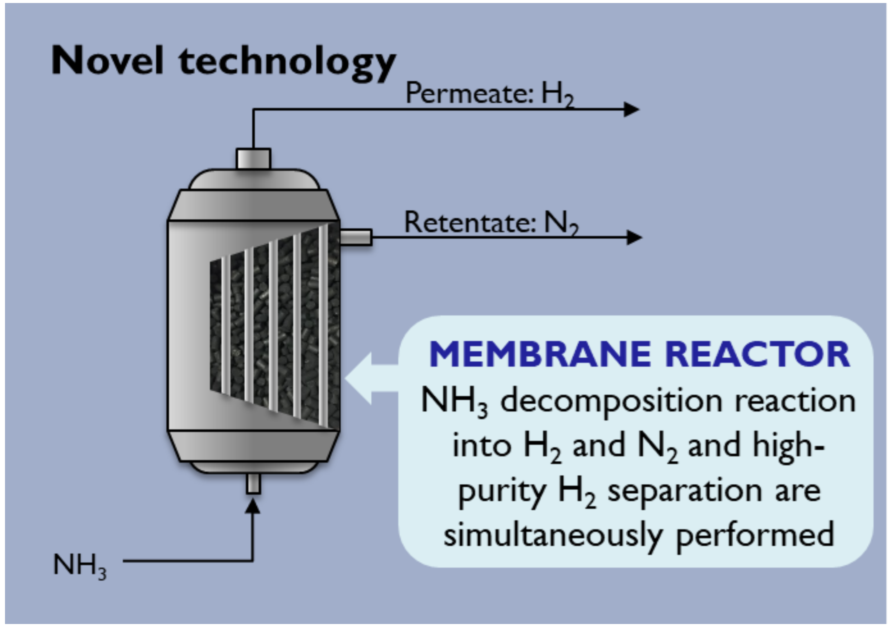
Ammonia decomposition

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

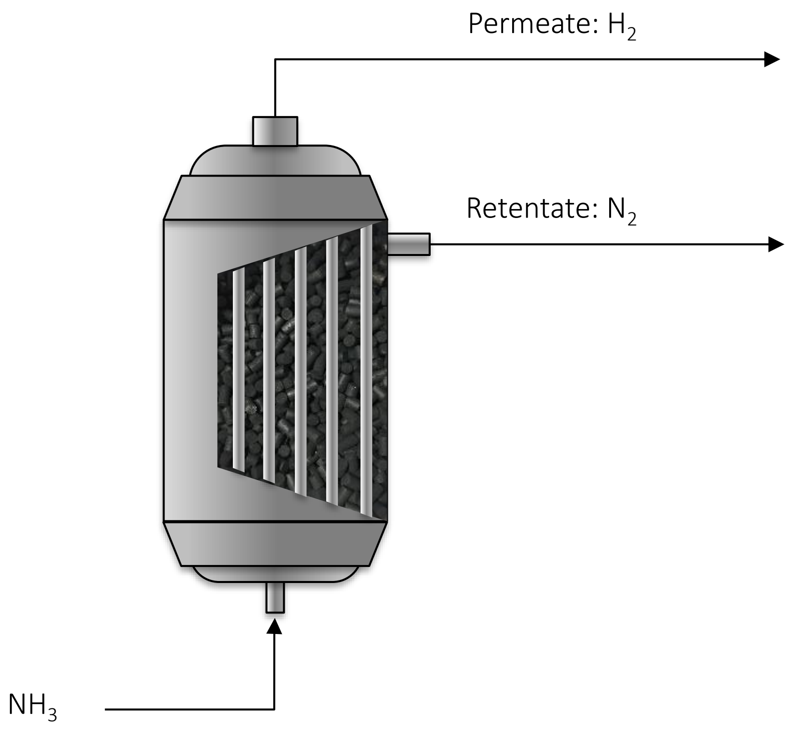
$$\Delta H_f^o = 45.9\ \frac{kJ}{mol}$$

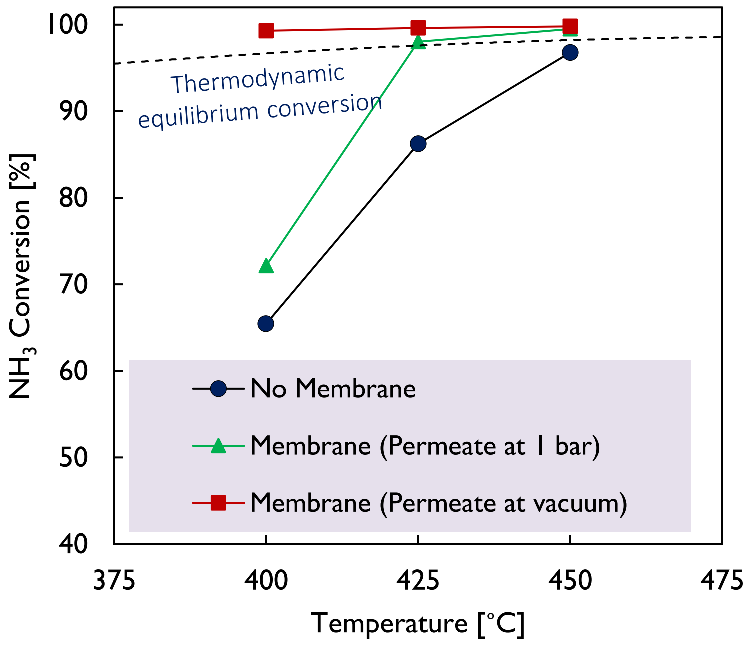


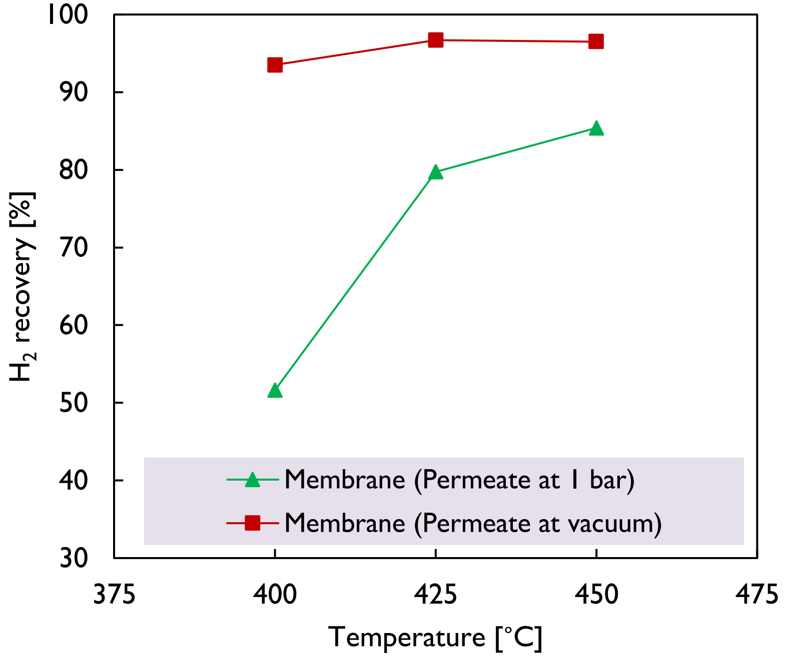




H_2 production via NH_3 decomposition in a catalytic membrane reactor





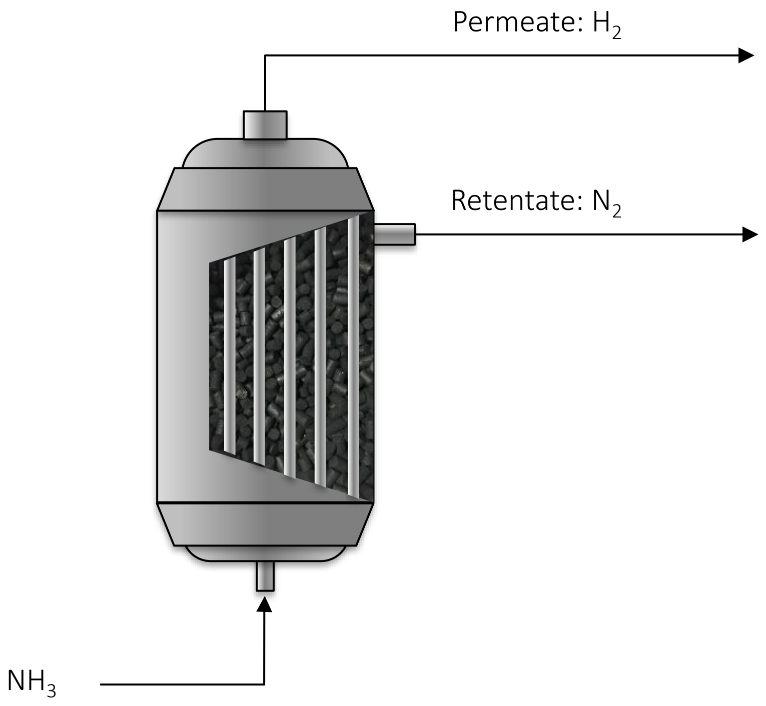


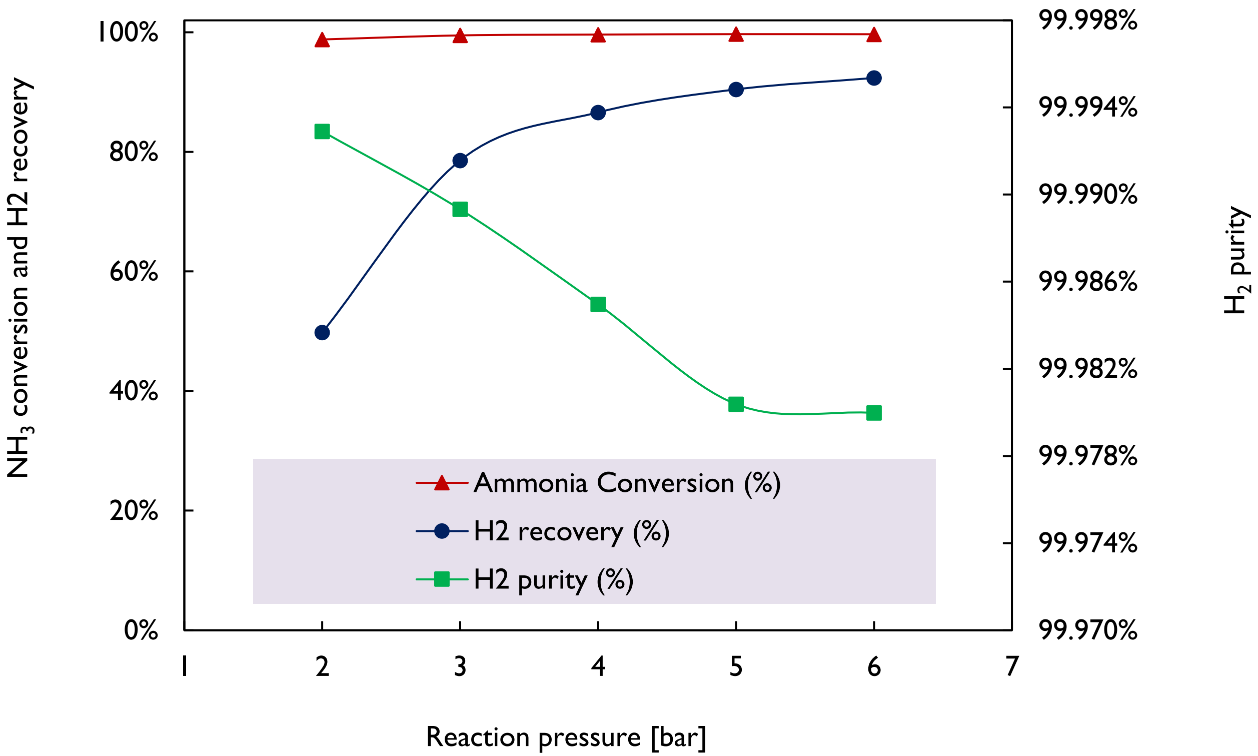
Experimental conditions	
ΔP [bar]	3
Permeate pressure [bar]	0.01-1
Feed flow rate [L_N/min]	0.5
Temperature [°C]	400 - 425 - 450

- Compared to conventional systems, in a membrane reactor:
  - Higher NH_3 conversion can be achieved at lower temperature (higher efficiencies)
  - High-purity H_2 is recovered
  - the footprint of the technology is reduced

9. Ammonia decomposition

H_2 production via NH_3 decomposition in a catalytic membrane reactor





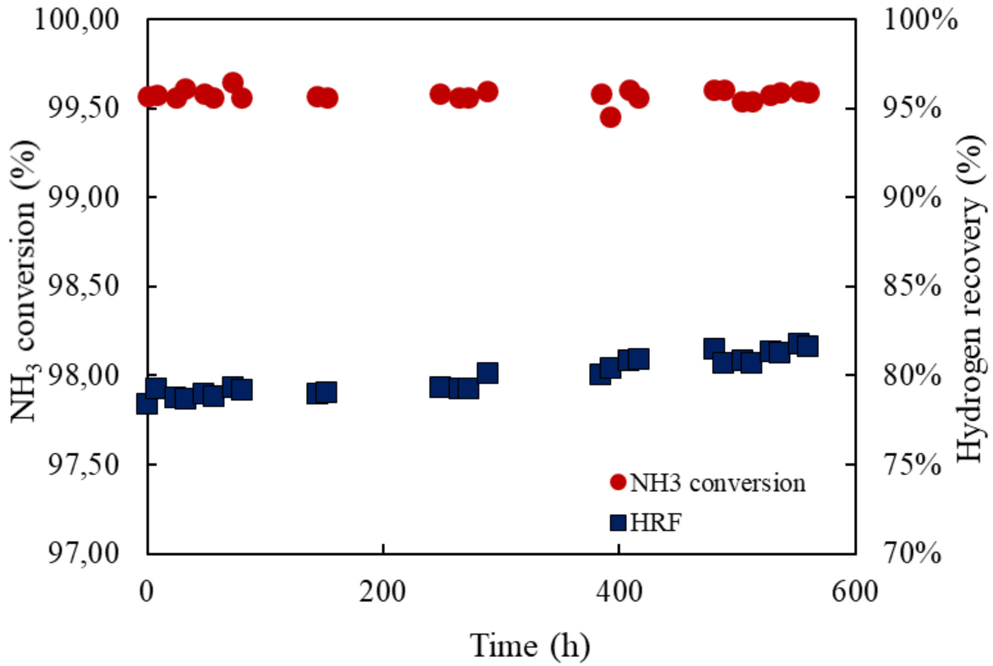
Experimental conditions	
T [°C]	450
Permeate pressure [bar]	0.01-1
Feed flow rate [L_N/min]	0.5

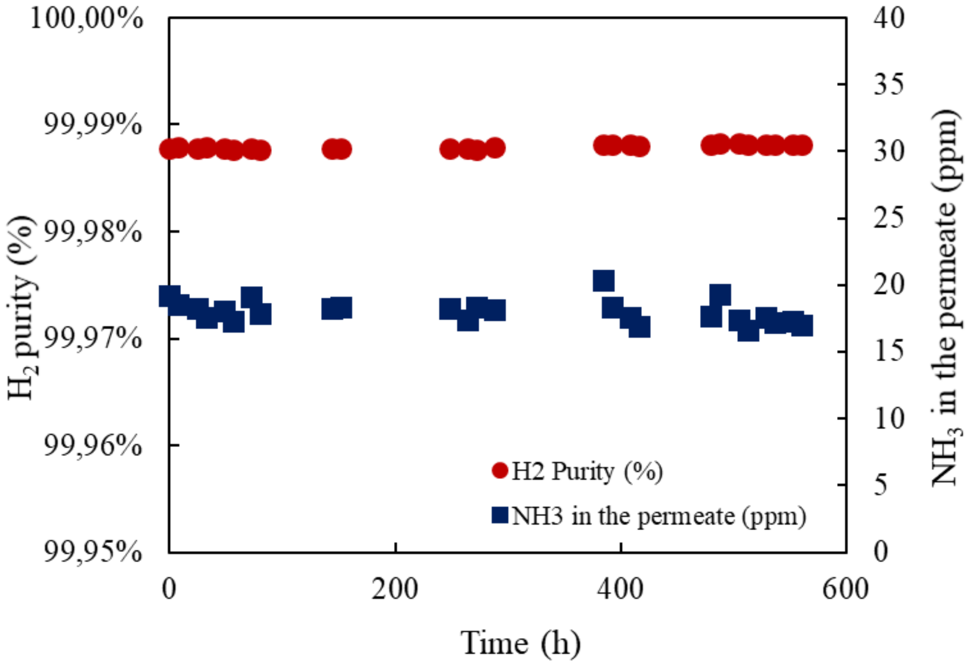
- Compared to conventional systems, in a membrane reactor:
  - Higher NH_3 conversion can be achieved at similar pressures (higher compactness)
  - Lower purities of H_2 recovered

9. Ammonia decomposition

H_2 production via NH_3 decomposition in a catalytic membrane reactor

Stability test





Stability test of the membrane reactor using the double sealing membrane for reaction carried out at 450 °C, 3 bar(a), 0.5 L_N/min of ammonia and the permeate at atmospheric conditions. The experimental results have been obtained with a Pd-based membrane with double sealing configuration.

- The process performance resulted to be stable over time.
- No decrease in the hydrogen purity, neither in the amount of hydrogen recovered were observed.

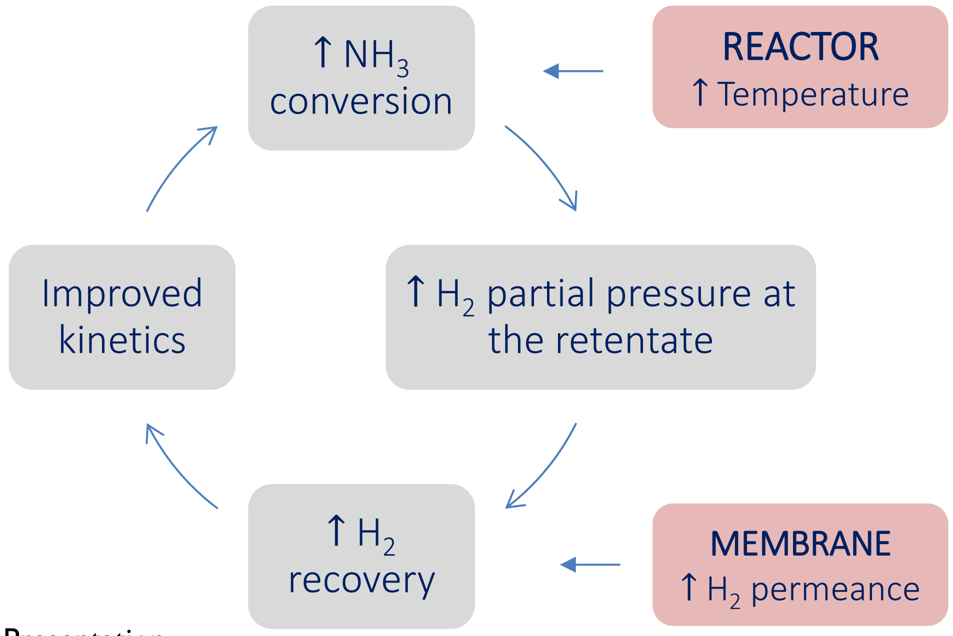
9. Ammonia decomposition

Effect of membrane's separation properties on the performance of a MR for NH_3 decomposition

Membrane	Selective layer thickness [μm]	H_2 permeance [mol/s/m²/Pa]	N_2 permeance [mol/s/m²/Pa]	H_2/N_2 perm-selectivity [-]
M1	~ 4–5	$1.64 \cdot 10^{-6}$	$3.47 \cdot 10^{-11}$	47080
M2	~ 1	$2.22 \cdot 10^{-6}$	$4.26 \cdot 10^{-10}$	5210
M3	~ 6–8	$1.15 \cdot 10^{-6}$	$1.66 \cdot 10^{-11}$	68960
M4	~ 6–8	$1.22 \cdot 10^{-6}$	$1.70 \cdot 10^{-11}$	71888
M5	~ 4–5	$2.18 \cdot 10^{-6}$	$2.18 \cdot 10^{-11}$	103000

- A higher thickness of the PdAg layer leads to:
  - lower H_2 permeance
  - Lower H_2/N_2 selectivity

The reactor's performance is optimized by tuning:
- membrane separation performance
- installed membrane area
- reactor operating conditions

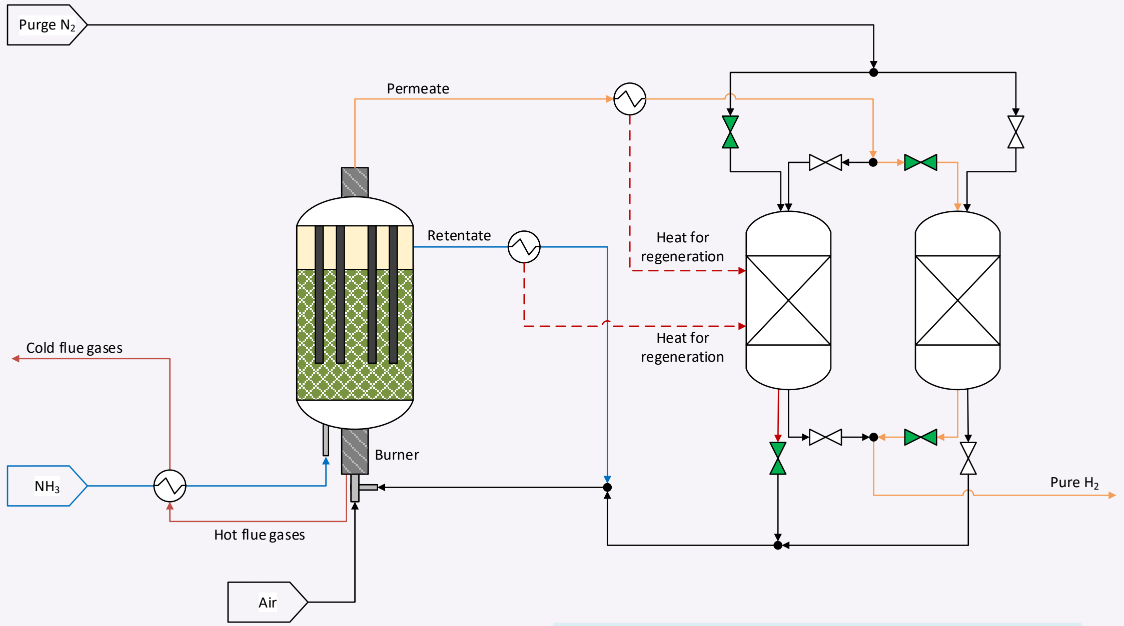


H_2 production via NH_3 decomposition in a catalytic membrane reactor

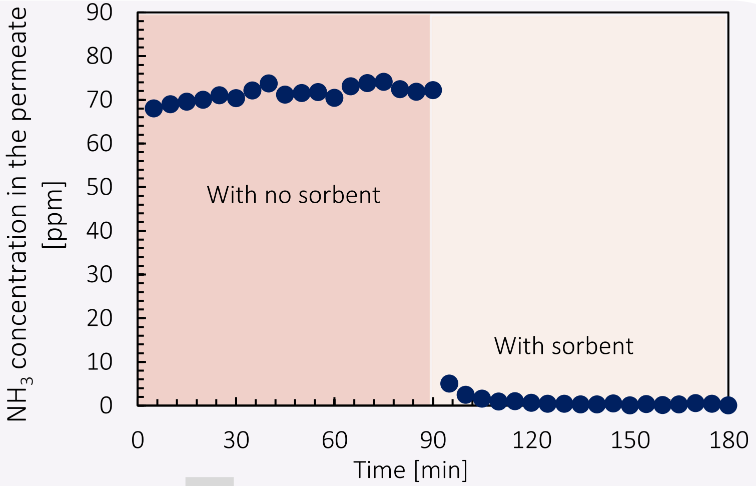
PEMFC specifications requires residual NH_3 concentration in the H_2 feed < 0.1 ppm.

Strategy 1: increase of membrane selectivity by increasing the membrane thickness
Strategy 2: implementation of a cleanup unit downstream of the MR implementing thin membranes

Both the strategies are technically feasible → Strategy 2 is more economically viable



↓ Thickness → ↑ Permeation → ↓ Pd for membrane fabrication ↓ Number of membranes



The reactor can be operated at lower temperatures with higher residual NH_3 concentration:

- Higher energy efficiency
- Less selective membranes to be implemented

9. Ammonia decomposition

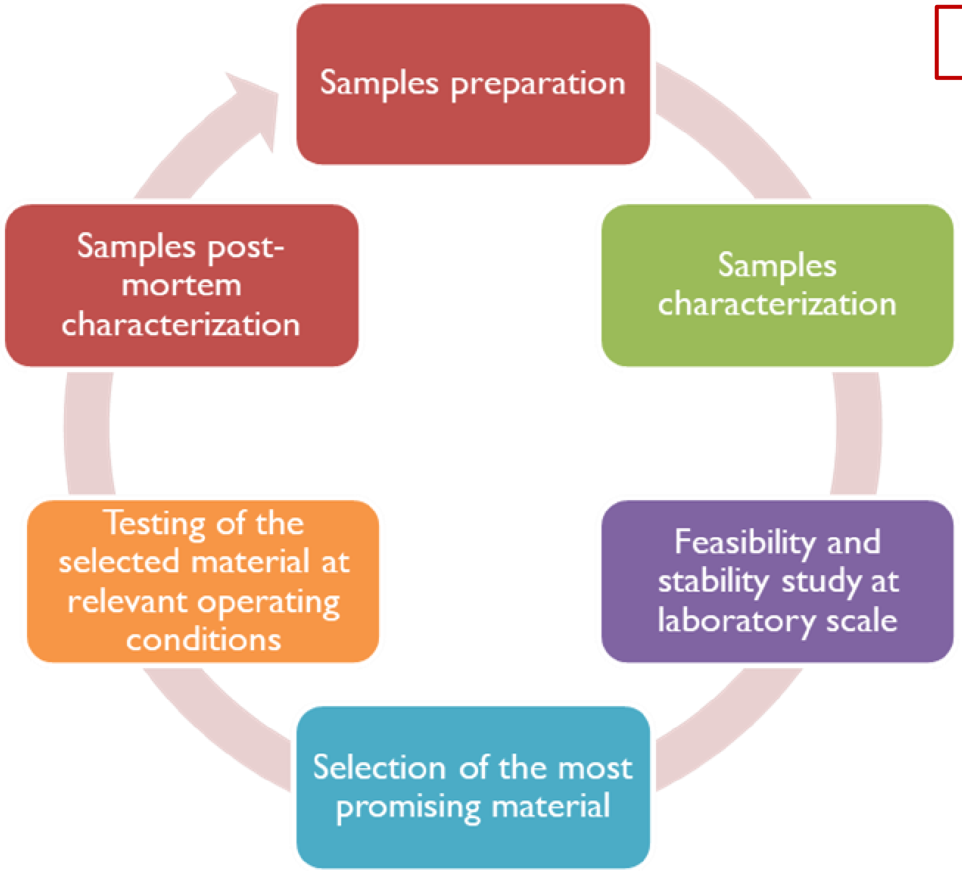
Sorbents for the H_2 cleanup: NH_3 removal

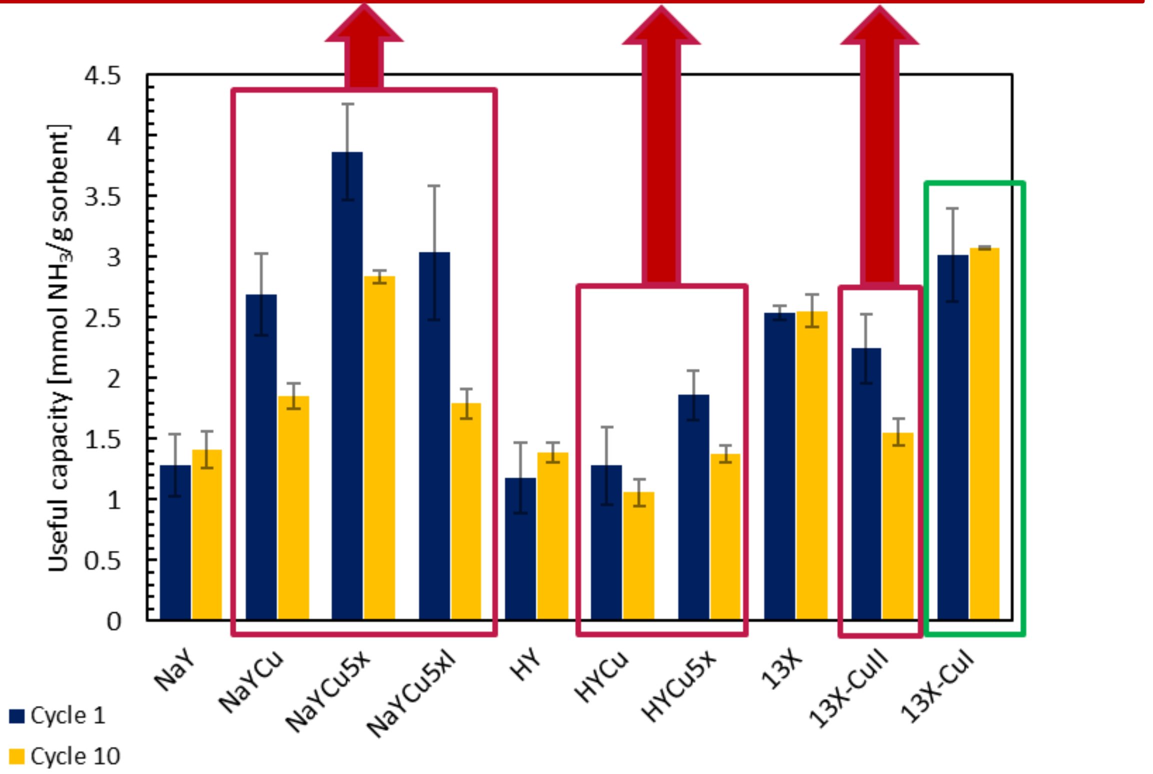
No study available in literature evaluates the H_2 cleanup from NH_3 for NH_3 concentrations that are relevant for the investigated applications

Investigation of Cu-exchanged form of Faujasite (FAU)-type zeolites
- Large pore size
- High acidity
- Large number of exchangeable cations

✓ NaY
✓ HY
✓ 13X

Deactivation due to aluminum migration as well as to Cu and Al agglomeration

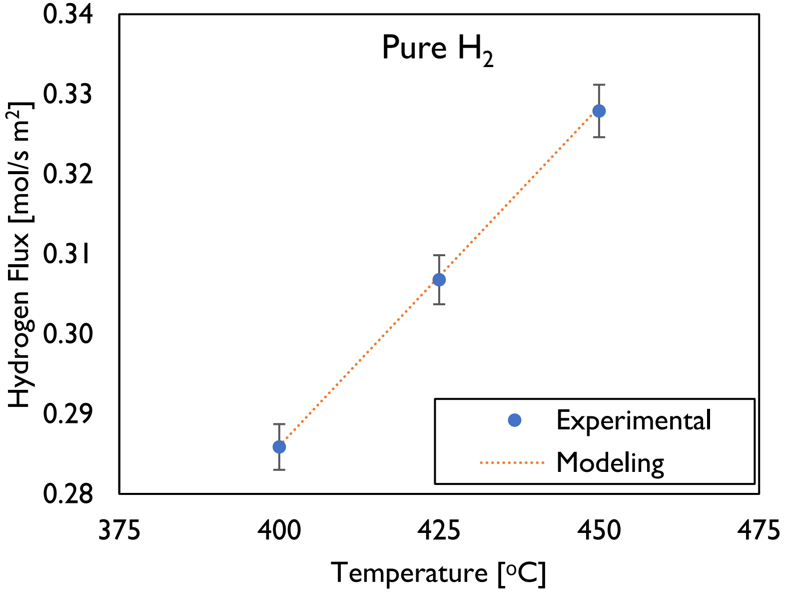


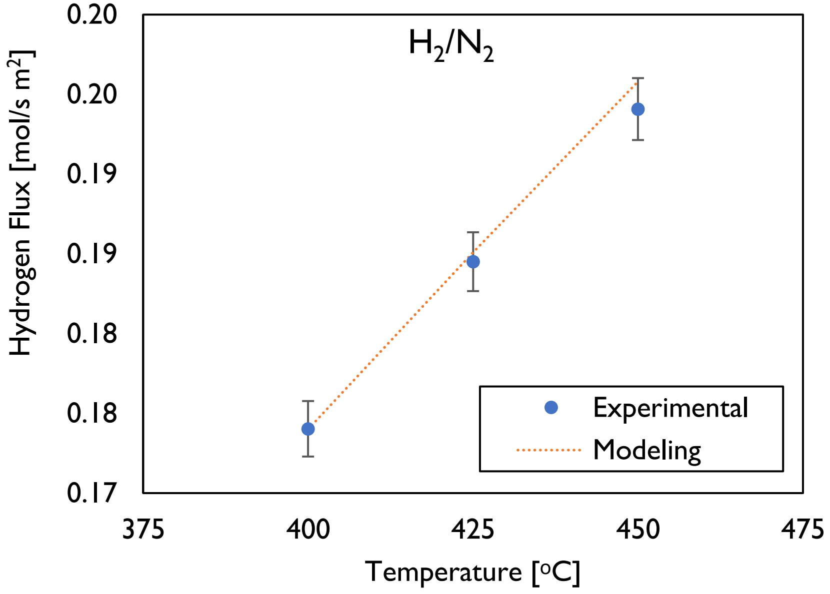


9. Ammonia decomposition

Modelling of a Pd-based MR for NH_3 decomposition

Membrane permeation modelling





✓ Errors<1%

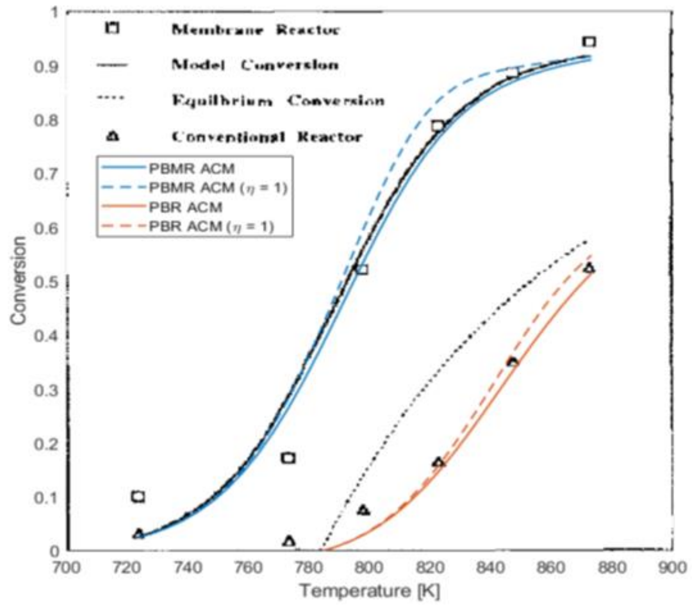
Good model prediction of flux under mass transfer limitation

MR modelling

- Concentration polarization on the retentate side

$$N_{H_2,R^*} = k_g C ln\left(\frac{P - P^*_{H_2}}{P - P_{H_2,bulk}}\right) = P_m\left(P^n_{H_2,ret*} - P^n_{H_2,perm}\right)$$

$$k_g = f\left(Sh, D_{H_2 i}\right)$$



9. Ammonia decomposition

Ammonia decomposition prototype

Membranes and catalyst for the ammonia decomposition prototype

- Pd-based membranes
    - 50 ds- Pd-based supported membranes
    - Electroless plating
    - Finger-like or open-end alumina supports
    - Average length: ~ 45 cm long
    - Membrane area: ~1 m^2
- Catalyst: Commercial Ru based catalyst

9. Ammonia decomposition

Ammonia decomposition prototype

Design & Construction of the ammonia cracker

- Main challenges:
  - Hydrogen piping & equipment requires high quality welding and thorough testing.
  - Membrane reactor needs to be accessible for membrane replacement: a manual ATEX rated hoist was installed to bring the reactor out of the container.
  - Small bore piping and tubing cannot take the weight of valves and instrumentation; special attention had to be paid to supports.
  - High temperatures require well designed and installed insulation.

Testing and validation of the ammonia decomposition prototype

Operation of the ammonia cracker

- CNH2 operated the cracker
- H2Site provided onsite training and remote monitorization via H2Site's remote Control Room.
- Great communication between both teams.
- Main challenges:
  - Nitrogen pressure
  - Ammonia composition
  - Low temperature in separation
  - Daily start-up and shut down

9. Ammonia decomposition

Testing and validation of the ammonia decomposition prototype

Operation of the ammonia cracker

- Nitrogen pressure: The system was designed to work at 8-10 bar, also during heating.
  - Available nitrogen in Fertiberia is 5 bar, so in order to overcome the pressure drop of the system, Nitrogen flow had to be reduced, which made heating slower.
    - Heating was supposed to be less than 4 hours, but it took around 6.
  - This would have prevented testing, because by the time the equipment was hot it was time to shut down for the day.
    - CNH2 reorganised working hours to work longer days so that testing could be done.
- Ammonia composition and pressure:
  - There are 2 sources of ammonia nearby: low pressure pure ammonia or high pressure "top of the tank" ammonia.
  - Top of the tank ammonia contains all the volatile contaminants in the manufacturing process, with varying composition, such as CH_4, CO_2, N_2 or Ar.
  - Ammonia pressure was 7 bar in the inlet, which made the separator work at around 5 bar.

9. Ammonia decomposition

Testing and validation of the ammonia decomposition prototype

Operation of the ammonia cracker

- Low temperature in separation:
  - The heat transfer expected with pure ammonia was better than with the "top of the tank" ammonia, which implied the temperature in the membranes was around 370°C, instead of the design 400°C.
  - Considering that only 70% of the inlet was ammonia, and that the separator was working at 5 bar and 370°C (instead of 8 bar and 400°C), the Hydrogen flowrate produced was smaller than the design:

Design	Design	Operation	Simulated for operation conditions
Ammonia purity (mol%)	99,99%	60-70%	60%
Membrane temperature	400ºC	370ºC	370ºC
Membrane pressure	8 bar	5 bar	5 bar
Hydrogen flow rate	0,91 kg/h	0,21 kg/h	0,288 kg/h

9. Ammonia decomposition

Testing and validation of the ammonia decomposition prototype

Operation of the ammonia cracker

- THE ISSUE: Daily start-up and shut down
  - System is designed for 24/7 operation, but had to be operated 10/4, instead.
  - Shutdown procedure was modified to try to reduce heating time and optimise operation time:
    - This led to membrane damage.
    - NH_3 entered the vacuum pump and damaged it.
  - Both the vacuum pump and the membranes had to be changed.
  - The Shutdown procedure was corrected to the original to avoid this issue from happening again.
  - The prototype was started again.

9. Ammonia decomposition

Testing and validation of the ammonia decomposition prototype

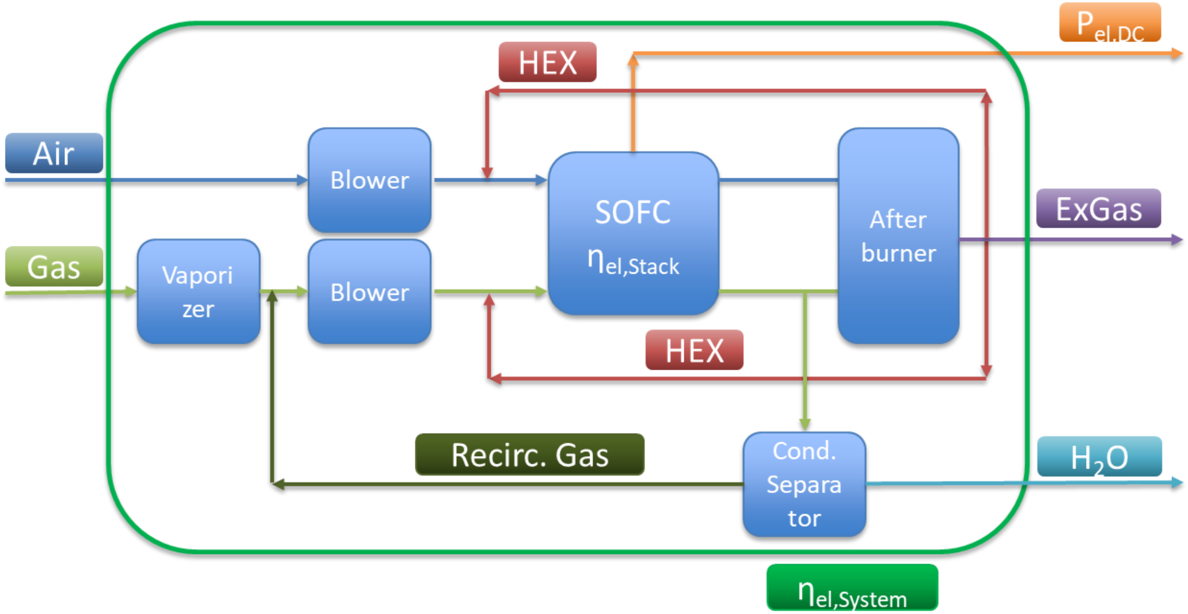
Lessons learnt

- Pressure drop throughout the system can increase heating time if the required pressure nitrogen is not available.
- Oversizing heating capacity could compensate for temperature loss in the membrane reactor, to ensure it works under design conditions.
- Shutdown operation is critical for membrane health.
- Thermal cycles (starting and stopping everyday) reduce the purity of the hydrogen.
- Everything is easier with a motivated and willing team, such as the one we found in CNH2 and Fertiberia.
- The prototype has produced high purity hydrogen for 500 hours!

10. Direct use of ammonia: Power generation with SOFC

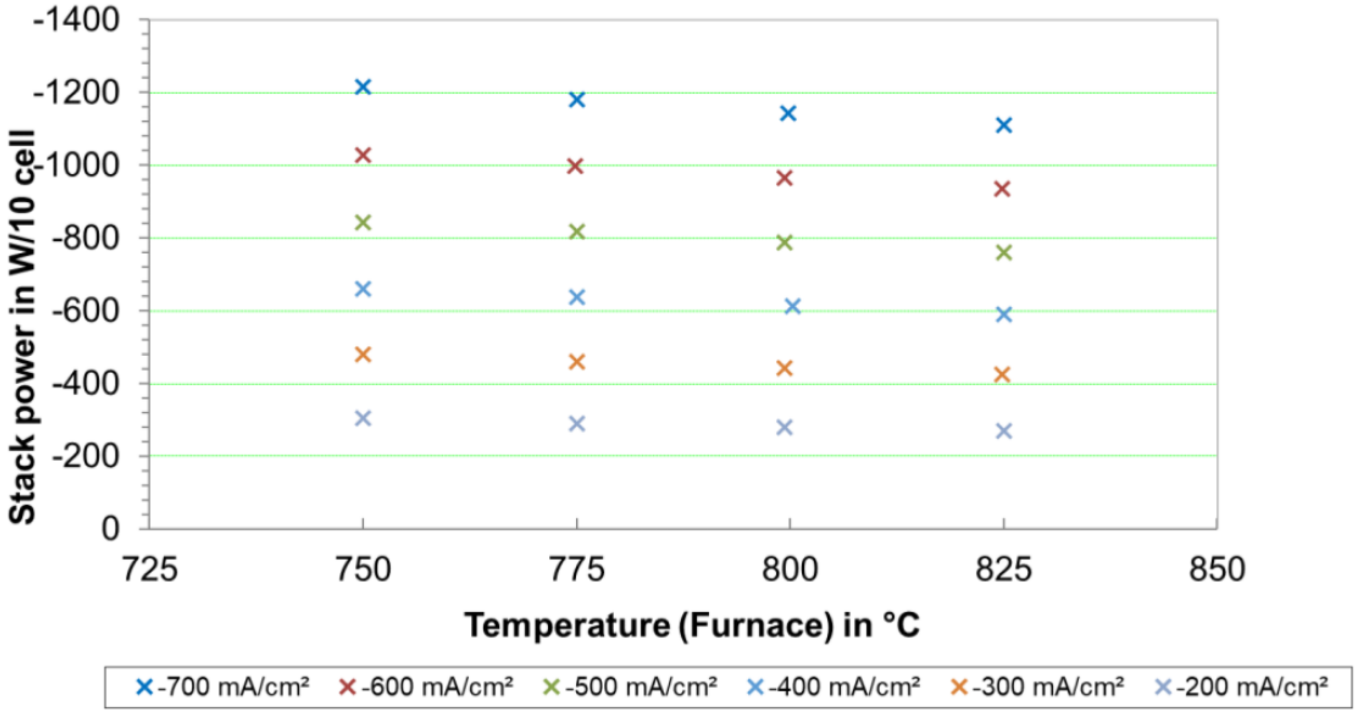
- Utilization of ammonia as fuel for SOFC
  - System evaluation
  - SOFC stack tests using ammonia
  - Check of NH_3 cracking inside preheaters
- Electric efficiency (DC):
  → 51% with CPOx
  → 60% with anode gas recirculation

→ Ammonia is a perfect CO_2 free fuel for SOFC



Performance map 10-cell-stack SOEC

- SOEC performance map 10-cell MK35x stack in steam electrolysis at 75% gas conversion at different temperatures



- Increased current density from -600 mA/cm² to -700 mA/cm²

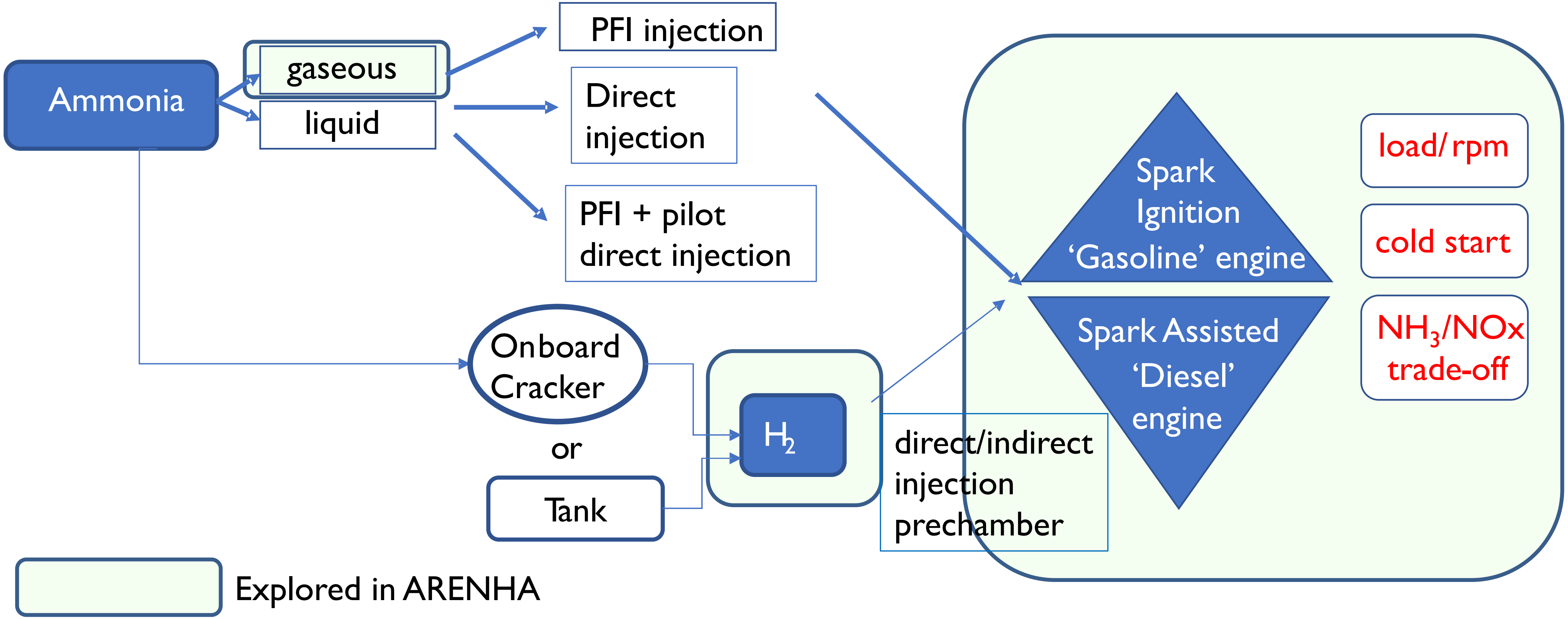
10. Direct use of ammonia: Power generation with SOFC

- MK35x stack for SOFC with wide temperature window 750-860°C
  - SOFC: up to 40 W/cell, NH_3 operation comparable to H_2/N_2 mixtures
- Ammonia cracks at stainless steel surfaces >600°C
- Efficient ammonia fueled SOFC systems possible with MK35x stacks
  - Less BoP: HEX at afterburner and no separate cracker, low blower power
- High temperature is a favor for NH_3 operation (low nitridification)

10. Direct use of ammonia: Internal Combustion Engines

Difficulties to auto-ignite NH_3 :

- spark ignition mode : optimum

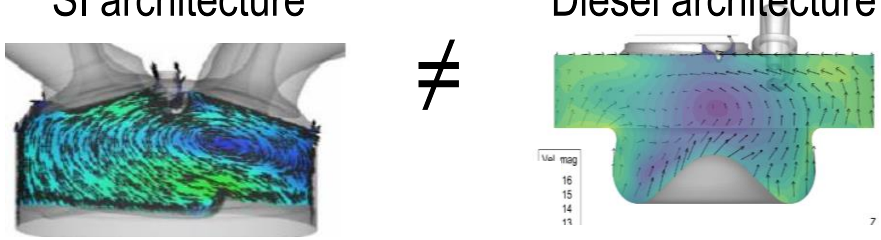


10. Direct use of ammonia: Internal Combustion Engines

Impact of engine architecture

- Objectives: assessment of combustion stability, efficiency, pollutants for pure NH_3
  - Identification of H_2 requirement
  - Specificity of 'cold start' conditions (650 rpm)
  - Identification of limits and tradeoffs (NOX versus NH_3)
- Different engines designs:
  - 2 standard engine : gasoline and diesel (but in single cylinder mode):
    - SI engine = 'current' EP6
      - regular Compression Ratio
    - SA Diesel engine = 'current' DV6 + spark plug instead of fuel injector
      - High Compression ratio : better for Ignition and Flame propagation
  - 1 research large stroke engine SI
    - SI engine with high CR

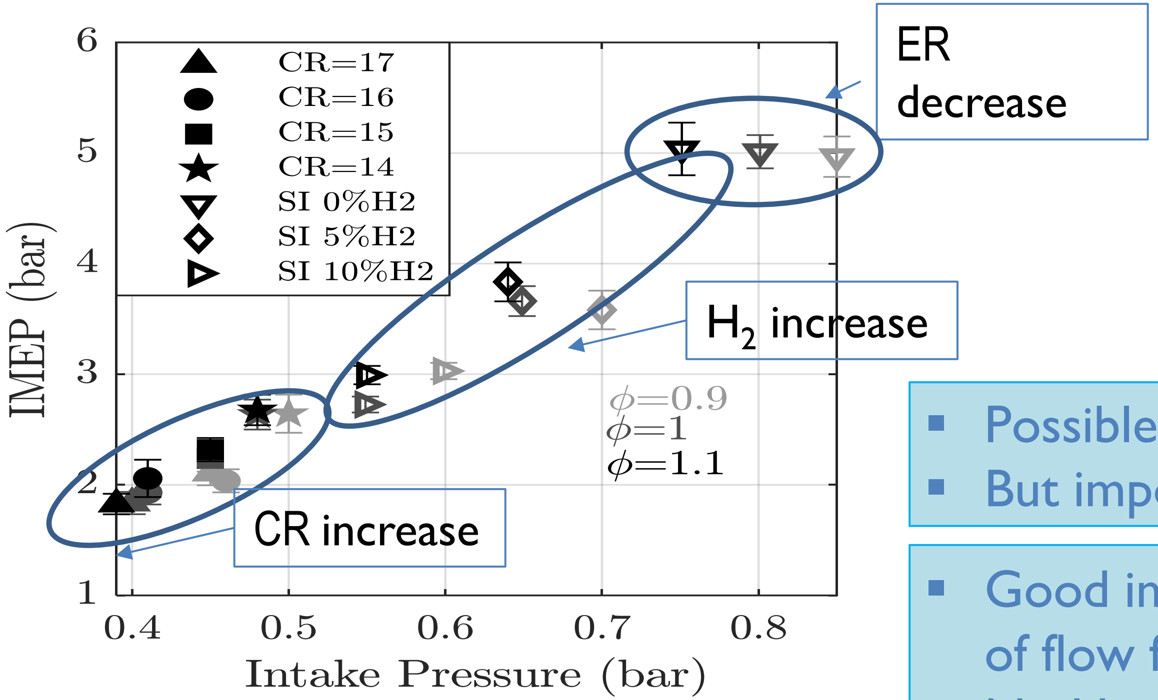
SI architecture ≠ Diesel architecture



10. Direct use of ammonia: Internal Combustion Engines

Impact of engine architecture

- Solution : Increase the CR to reach 'cold start' conditions



Engine speed :1000 rpm

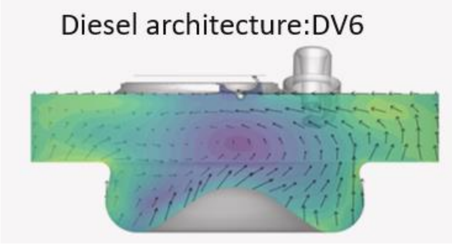
Engine Type	Gasoline engine PSA EP6DT	Diesel engine PSA DV6
Displacement Volume V_{cyl}	400 cm^3	400 cm^3
Compression Ratio	10.5	14 to 17
Valves	4	2
Tumble ratio	2.4	
Swirl ratio		2

- Possible to run without H_2 even with standard SI
- But impossible to reach stable conditions without H_2

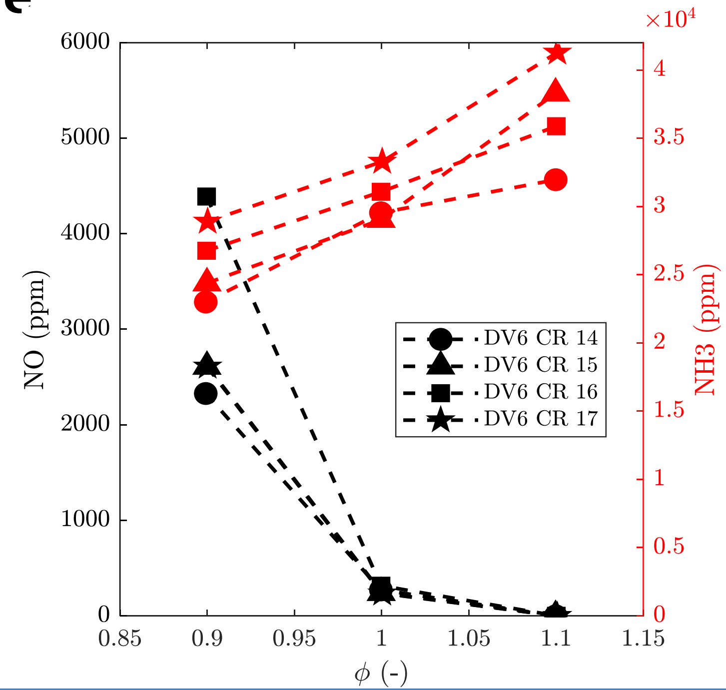
- Good improvement of NH_3 combustion with CR increase despite of flow field
- No H_2 needs
- Extension of low load limits
  - lower limit with slightly rich

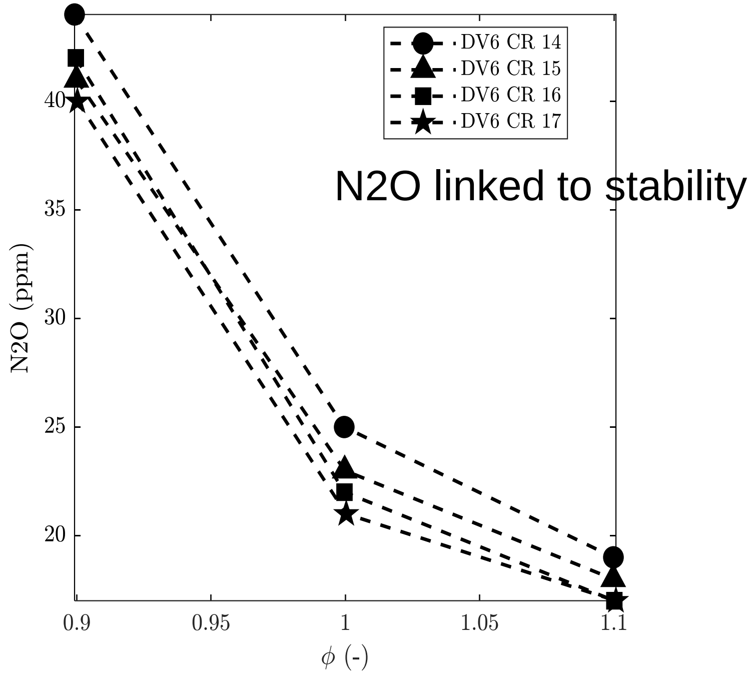
10. Direct use of ammonia: Internal Combustion Engines

Impact of engine architecture



NH_3 linked to trap area and cylinder pressure



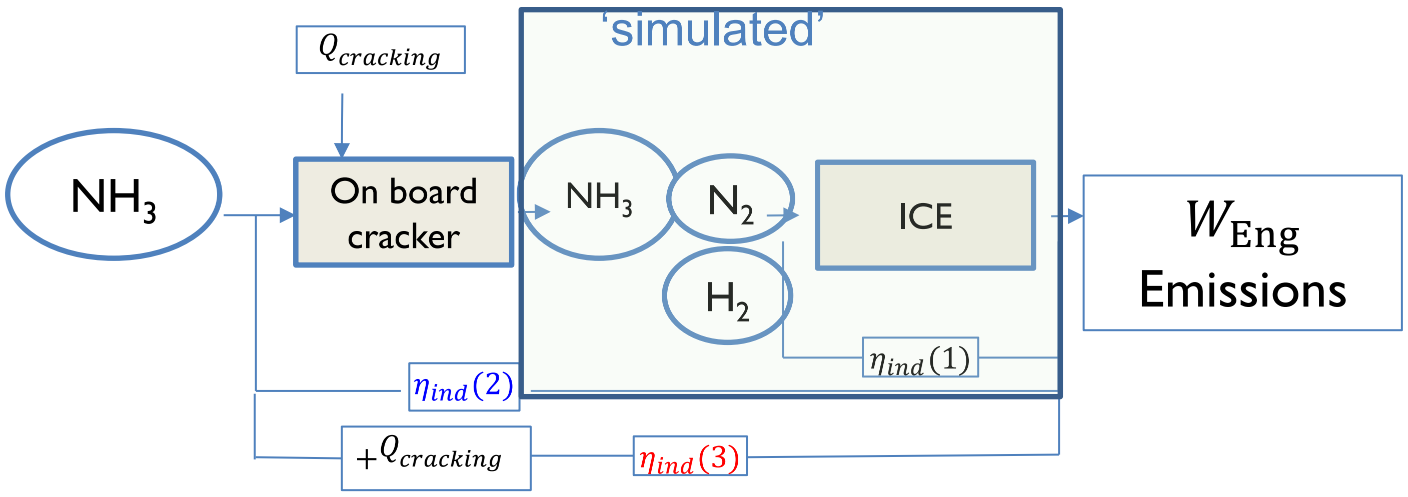


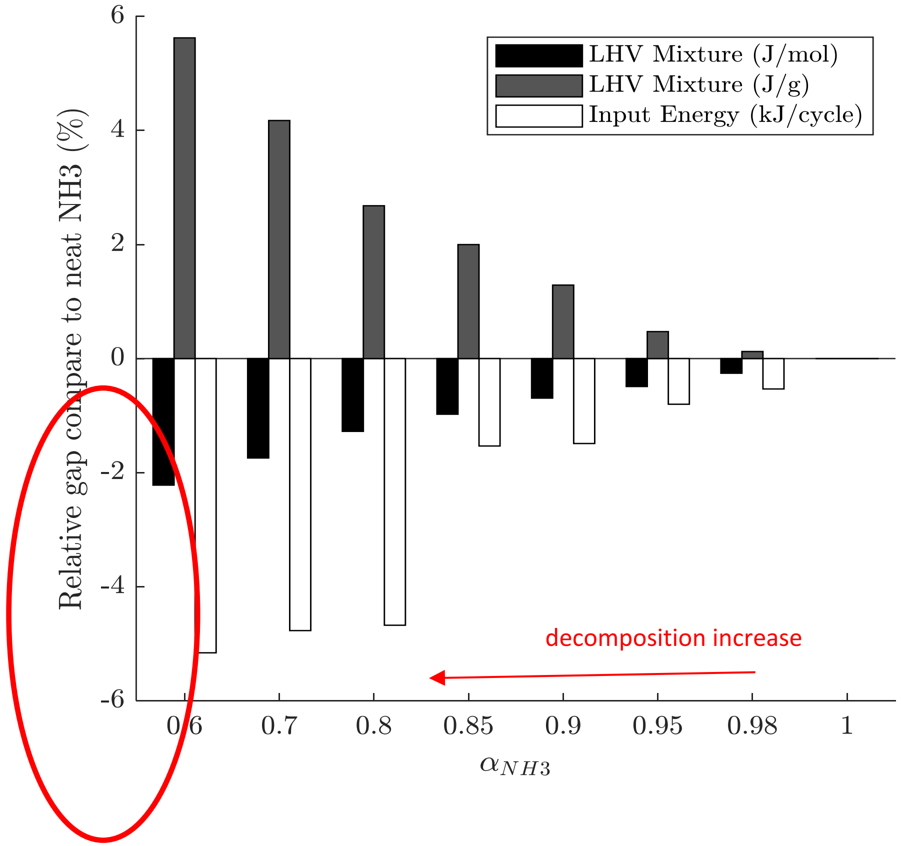
- **NO_x**
  - Minimum for **rich mixture**, Maximum around 0.7-0.8 until 5000 ppm !
  - Increase with H_2 addition
- **NH_3**
  - Minimum for **lean mixture/stoichiometry, max can be 4%**
  - **Function of engine design !**
  - **H_2 emissions due to 'in situ' decomposition of NH_3**

10. Direct use of ammonia: Internal Combustion Engines

Ammonia on-board cracking: benefits ?

$$\alpha NH_3 + (1-\alpha)\left(\frac{3}{2}H_2 + \frac{1}{2}N_2\right) + \frac{3}{4}(O_2 + 3.78N_2) \rightarrow \frac{3}{2}H_2O + \left(\frac{1}{2} + \frac{3}{4} * 3.78\right)N_2$$





10. Direct use of ammonia: Internal Combustion Engines

Ammonia on-board cracking: benefits ?

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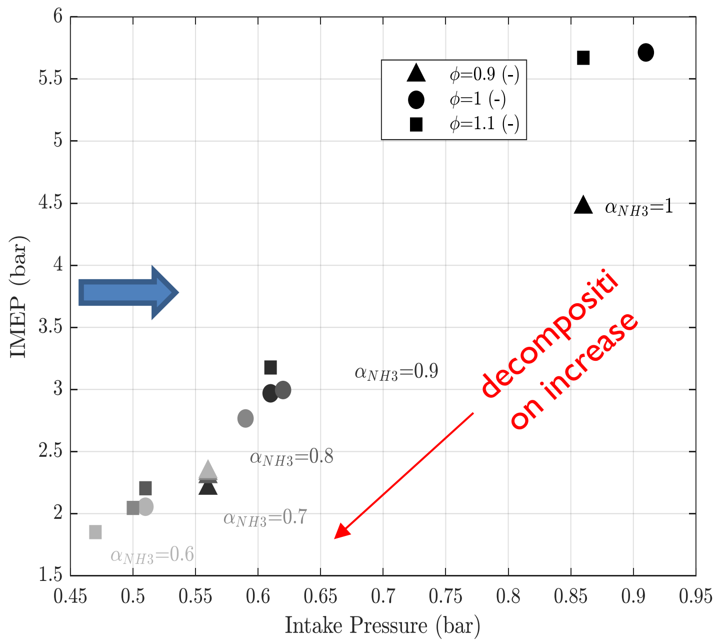
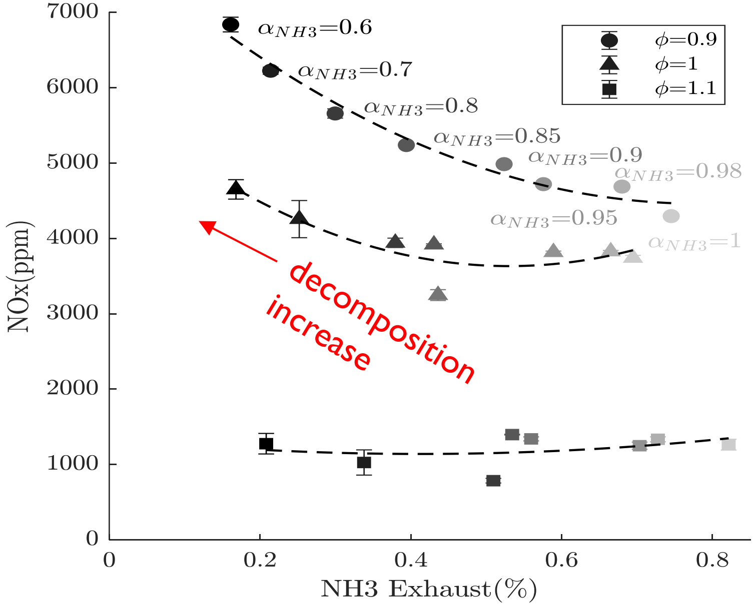




Best solutions to ensure engine start + to limit pollutant emissions

- ➢ small size cracker sufficient, 100% conversion non needed

10. Direct use of ammonia: Internal Combustion Engines

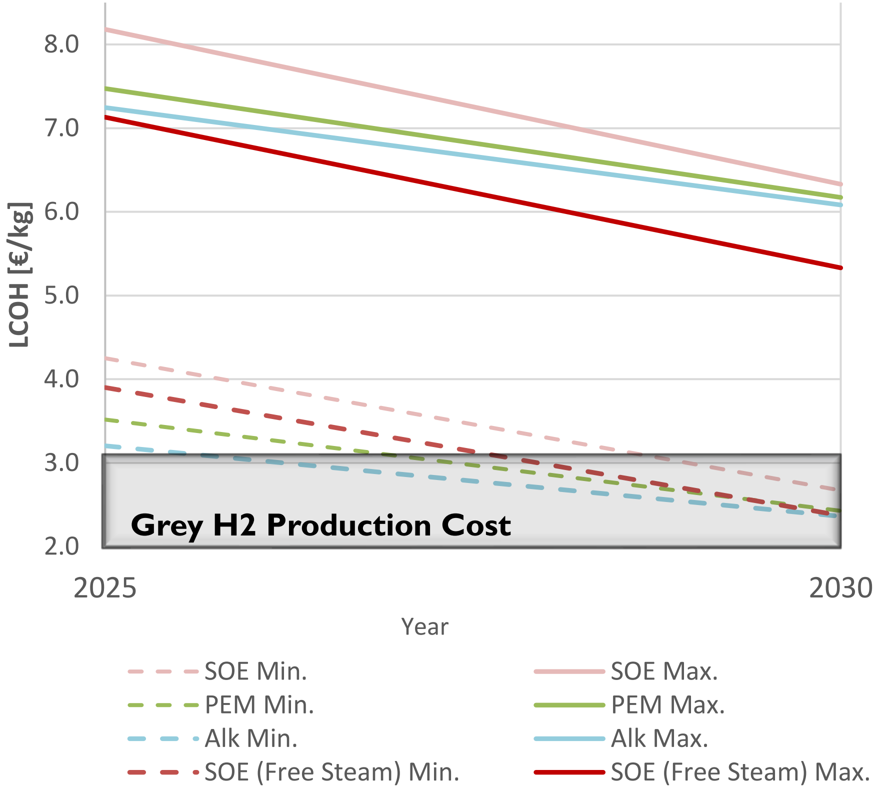
- GOOD NEWS :YES IT IS POSSIBLE !

- In standard Gasoline engine :
  - small contents of H_2 to guarantee all operating conditions
    - even with non-usual Compression Ratio !
  - means of 'small' reformer = optimisation not evident

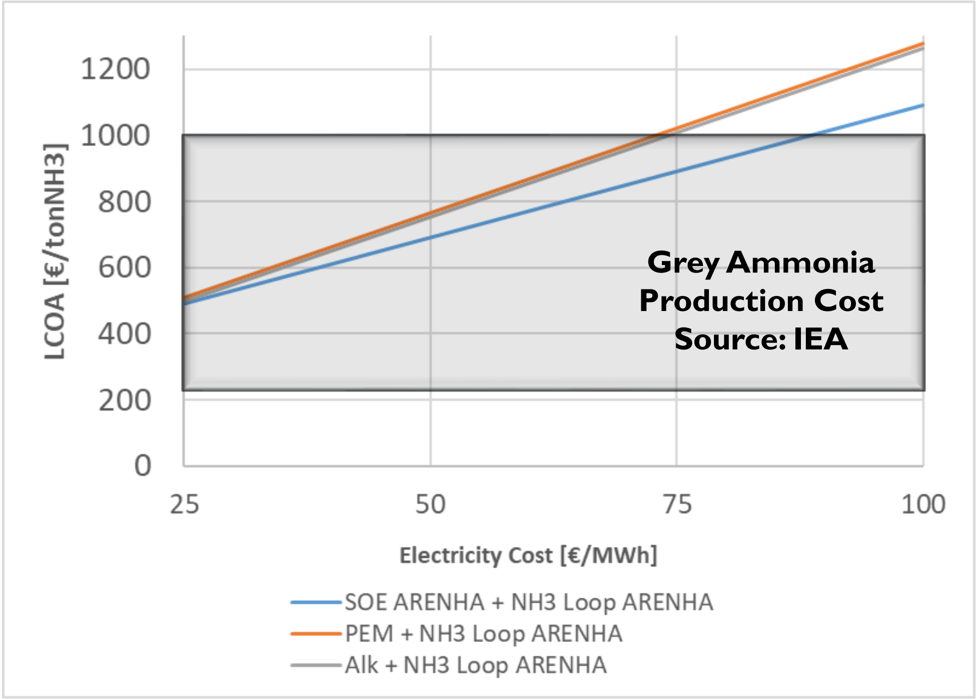
- In standard Diesel engine :
  - addition of spark plug = optimisation ?
  - more unburnt NH_3 and H_2 at the exhaust

Economic Assessment

- Techno-economic assessment of green hydrogen an ammonia production was carried out using developed models:



LCOH projection for Alkaline, PEM and Solid Oxide Electrolysis systems operated with 60% year average capacity factor. Min and max cases refer respectively to 25 and 100 €/MWh electricity cost. 30 years plant lifetime and 7% WACC assumed.



LCOA sensitivity carried out for ~300 tNH3/d Power-to-Ammonia based on SOE, Alkaline and PEM electrolysis technologies in 2030 scenario, 90% system availability, 30 years plant lifetime and 7% discount rate were assumed

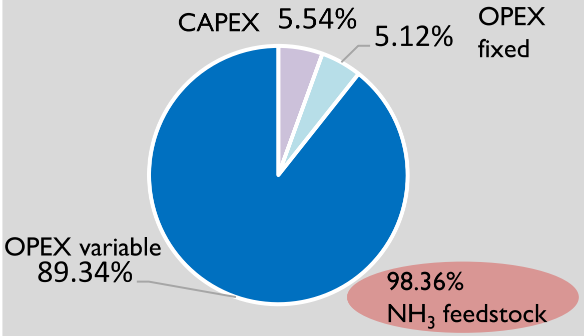
Economic Assessment

- Techno-economic assessment of Ammonia-to-Hydrogen for different scenarios was carried out using developed ammonia decomposition model:

On-board vehicle applications

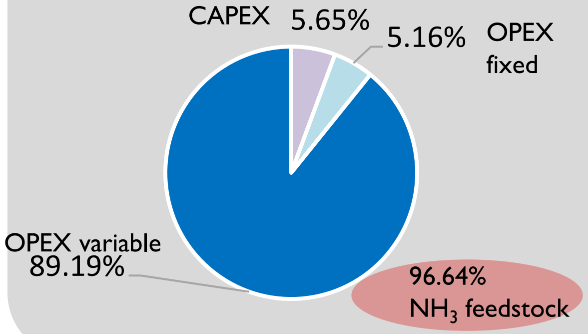
Conventional system

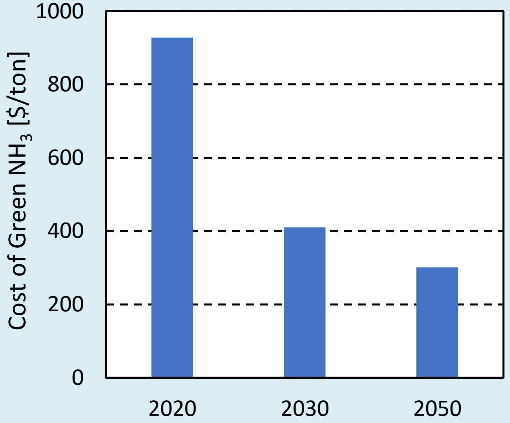
COH = 7.15 €/kg



Membrane Reactor assisted system

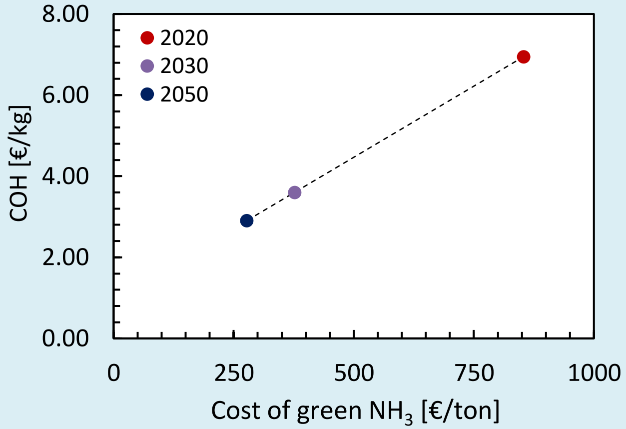
COH = 6.95 €/kg





https://www.iea.org/reports/global-hydrogen-review-2021/executive-summary

Year	Cost of NH_3 [€/ton]	COH [€/kg]
2020	853.92	6.95
2030	377.07	3.60
2050	277.30	2.90

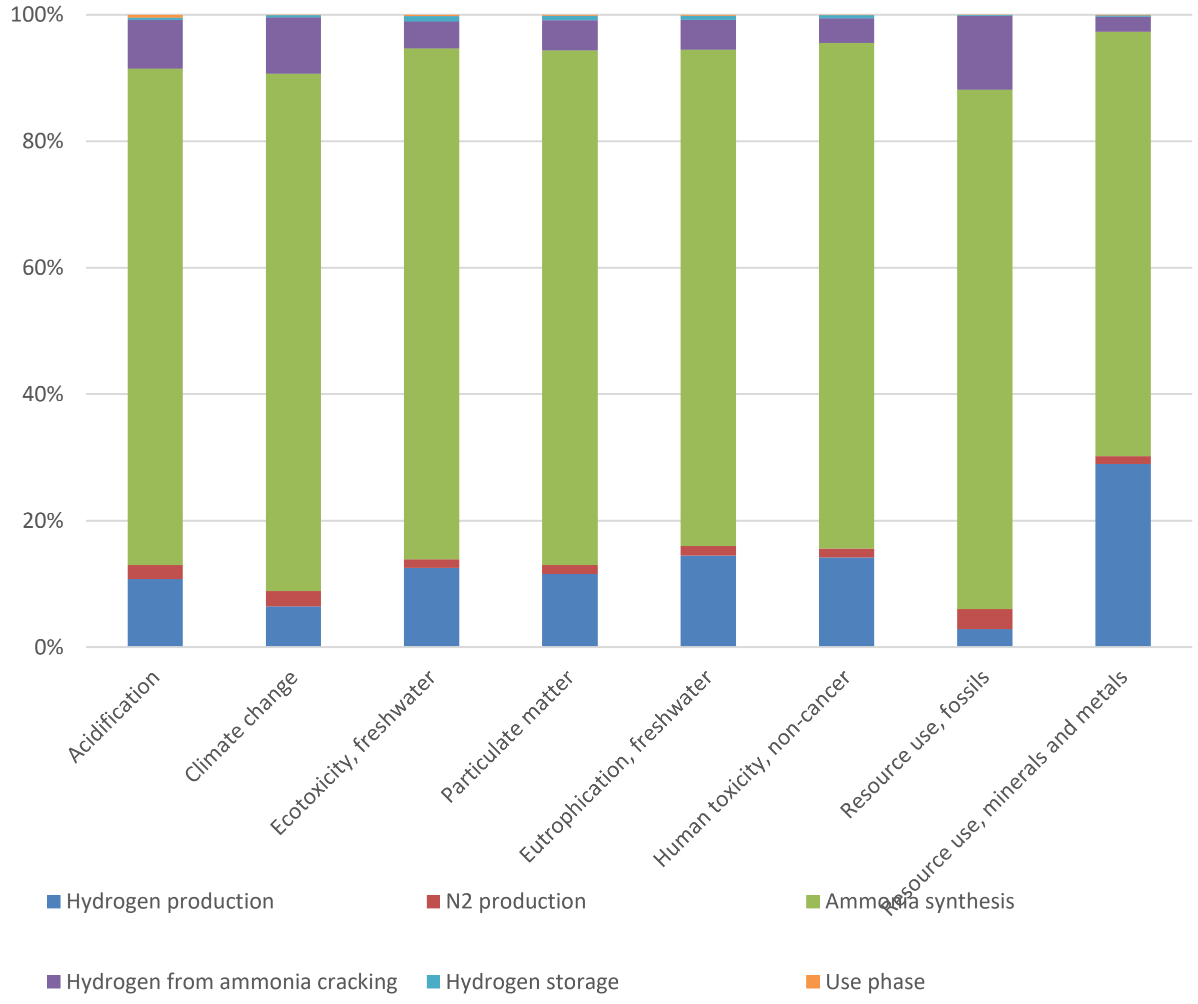


Environmental Assessment

- The environmental assessment of the ARENHA was been carried out through the Life Cycle Assessment (LCA) methodology. This approach is standardized (ISO 14 040 and 14 044) and provides the environmental impacts of a system through various indicators.
- The methodology was applied to different scenarios. First 4 scenarios were considered for the upstream sourcing: grey ammonia (ammonia from H_2 based on steam methane reforming), blue ammonia (grey ammonia associated with carbon capture) and green ammonia (ammonia from H_2 based on electrolysis from renewable electricity) and direct green H_2 production (no ammonia involved). Then, 2 use end cases were considered: production of electricity and mobility.
- The results are shown on various indicators: climate change, resource depletion or particulate matter (i.e. air quality)

Environmental Assessment

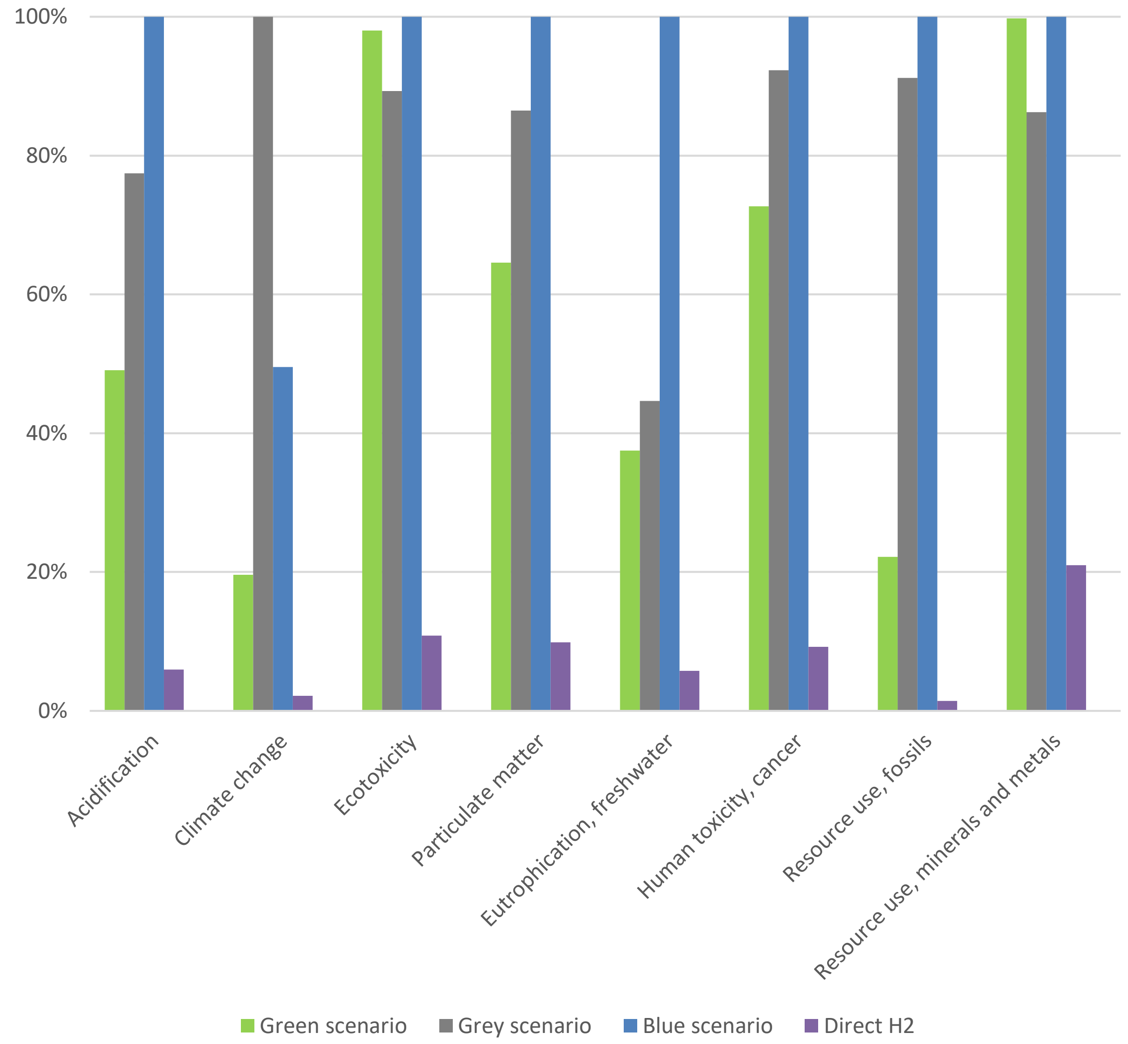
Contribution analysis for the electricity scenario based on green ammonia



- The ammonia synthesis and the hydrogen production are the most contributing steps.
- The impacts from the ammonia synthesis come from the electricity consumption. The Spanish electricity grid partly relies on the gas combustion.
- The steel container is also an important source of impact but the worst-case scenario was chosen.

Environmental Assessment

Comparison for the electricity scenario based on different sources for ammonia and direct H_2 use



- The most efficient scenario is the direct use of H_2 : as it demands less energy for conversion.
- In terms of ammonia production, the green scenario is globally the most interesting one.
- For climate change, the grey scenario induces direct CO_2 emissions during the SMR process. For the other indicators, the electricity consumption for the CO_2 storage is important to monitor.

11. Environmental LCA, economic and safety assessment

Conclusions

- In the reference scenario based on the use of green ammonia, the ammonia synthesis is the most contributing steps as it is based on Spanish electricity grid. If the national grid becomes greener through the years, the overall impacts will decrease.
- The direct use of hydrogen has less environmental impacts as it avoids multiple conversion steps that require energy.
- Green ammonia gives better environmental results compared to grey and blue ammonia.
- The ammonia chain is still at pilot scale. The LCA study provides relevant insights to optimize some parts of the process. An ammonia project at larger scale with more consolidated could lead to a decrease of the environmental impacts.

12. Dissemination and communication activities

- Project logo, leaflets, roll-ups, cards, and set of public document templates
- Public Project website: Home | ARENHA
- Dissemination and Communication Plan (updated on M6, M12, M30)
- First, Second and Third Public Presentations
- Nine issues of the 6-month Project Newsletter
- ARENHA dissemination activities (updated on M18, M36, M60)

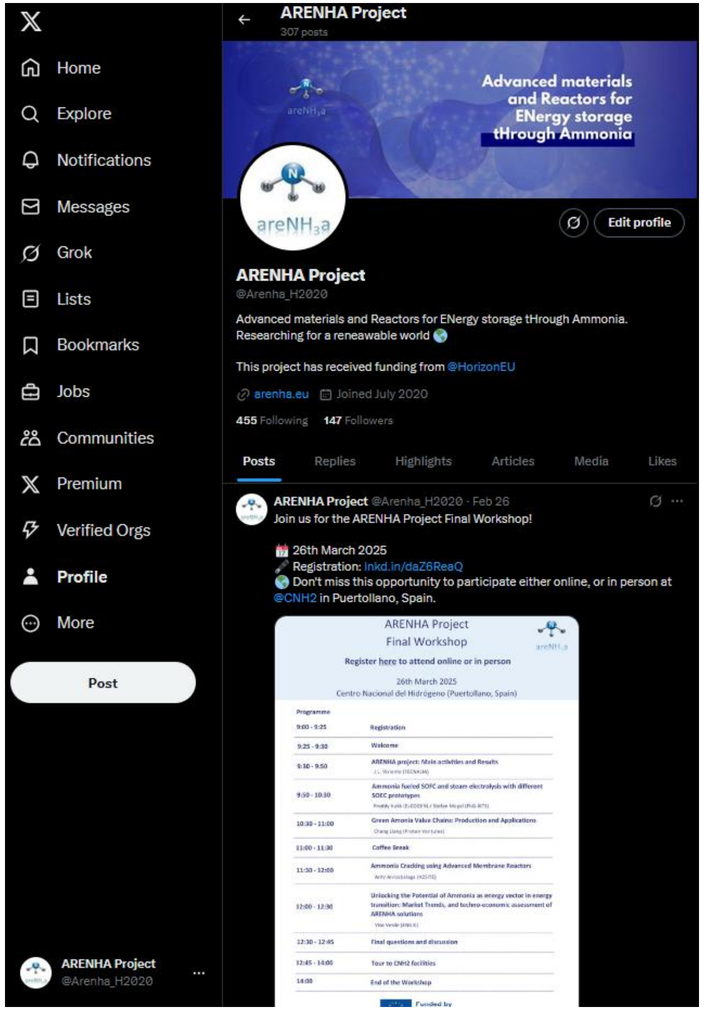
Overview of dissemination activities

Scientific publications	Conferences, Workshops	Patent requests	PhD Thesis	Newsletters	Videos	Press articles, radio	Workshops, webinars
13	42	3	1	9	3	17	3

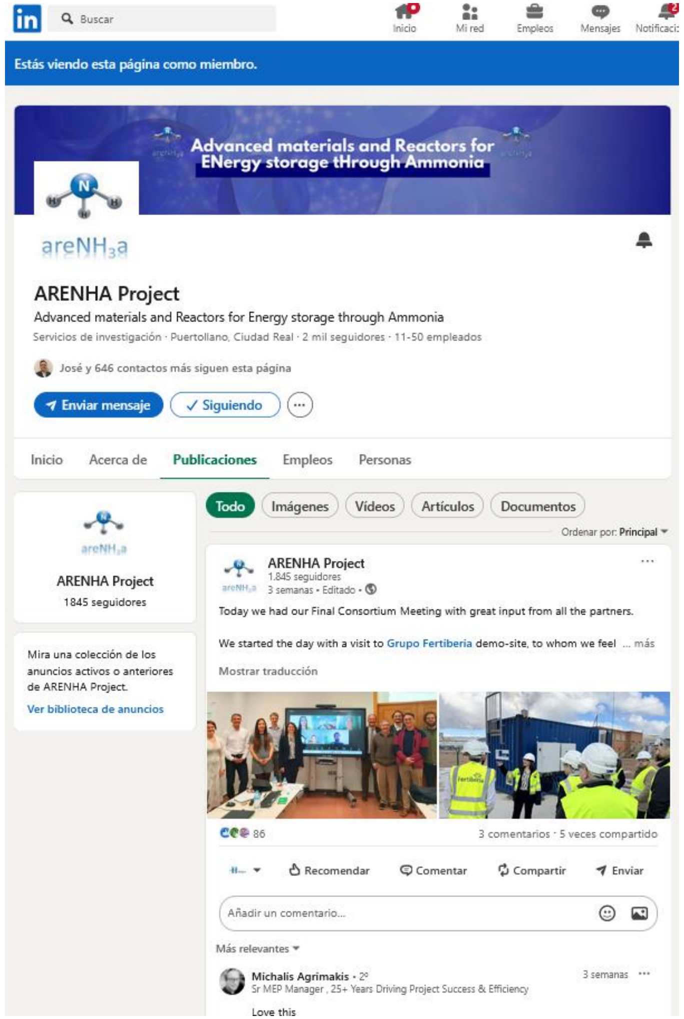
12. Dissemination and communication activities

- Social Media: 580 posts

X (~150 followers)



LinkedIn (~2000 followers)



13. Conclusions

- ARENHA has demonstrate the use of ammonia as green energy carrier with activities in the complete value chain: Power-to-ammonia-to-usage.
- Four prototypes developed in the frame of ARENHA:
  - Two 5 kWe SOEC stack modules
  - New ammonia synthesis loop
  - Ammonia decomposition system
- In future scenario, Solid Oxide Electrolysis technology has the potential to become competitive with low-temperature electrolysis technologies, especially in scenarios characterized by high electricity costs and waste heat availability for steam integration to the electrolyser.
- ARENHA integrated Power-to-Ammonia solution based on SOE could become competitive with low-temperature electrolysis-based solutions and traditional ammonia production pathway (this latter in case of low electricity costs and high system utilisation).
- The recovery of H_2 from green NH_3 (Ammonia-to-Power) using membrane reactors can be achieved at lower costs compared to the benchmark technology. The membrane reactor technology holds significant potential in advancing the decarbonization of the current energy system.

Advanced materials and Reactors for Energy storage tHrough Ammonia (ARENHA)

Thank you for your attention

https://arenha.eu/

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