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Advanced materials and Reactors for Energy storage tHrough Ammonia

ARENHA

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https://arenha.eu/

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Duration: 4 years. Starting date: 01 April 2020

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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

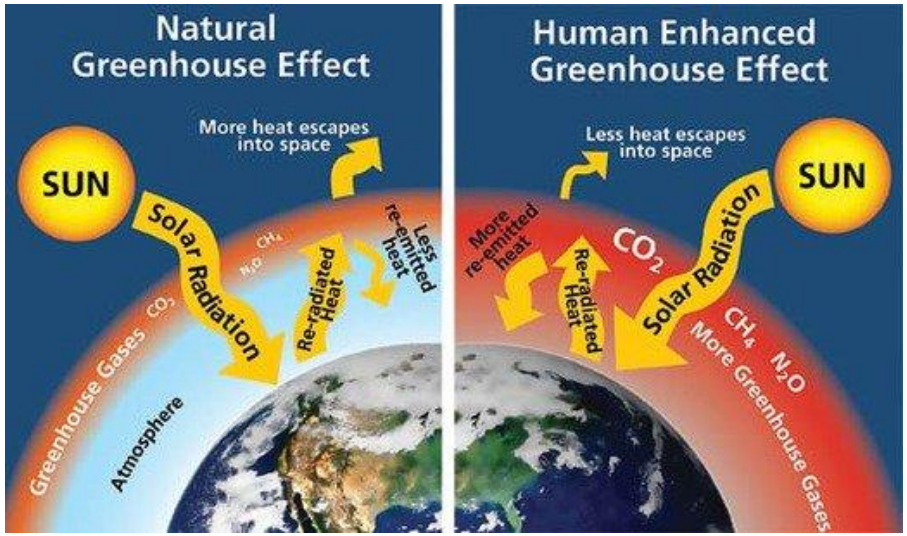
Greenhouse gasses

- **Effect**

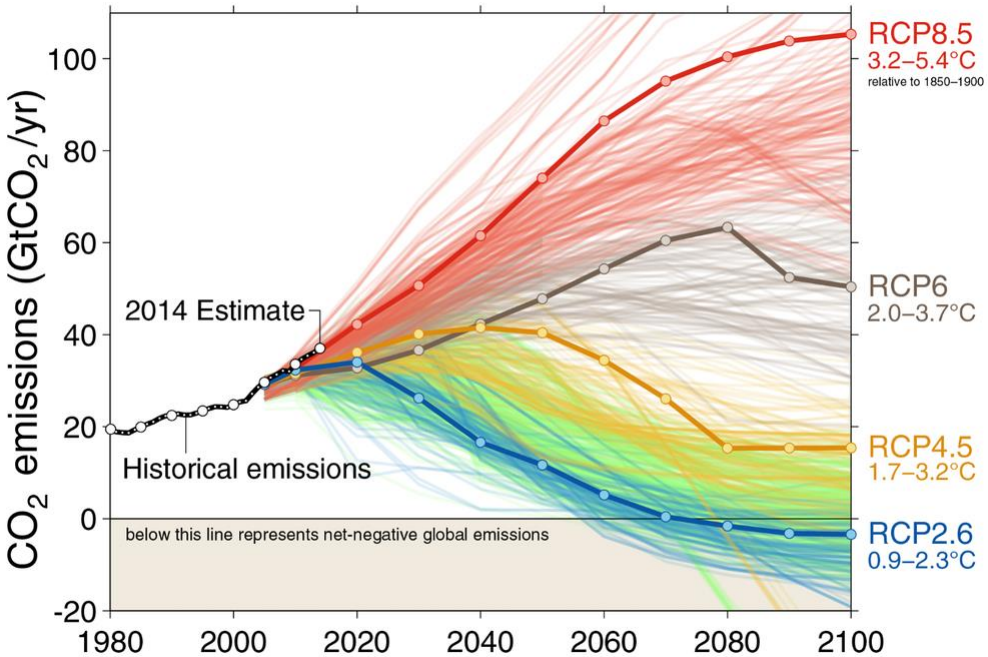
  Trap IR-radiation (heat)

- **Emission CO_2**

  Natural & human activity



1. Introduction



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

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.

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

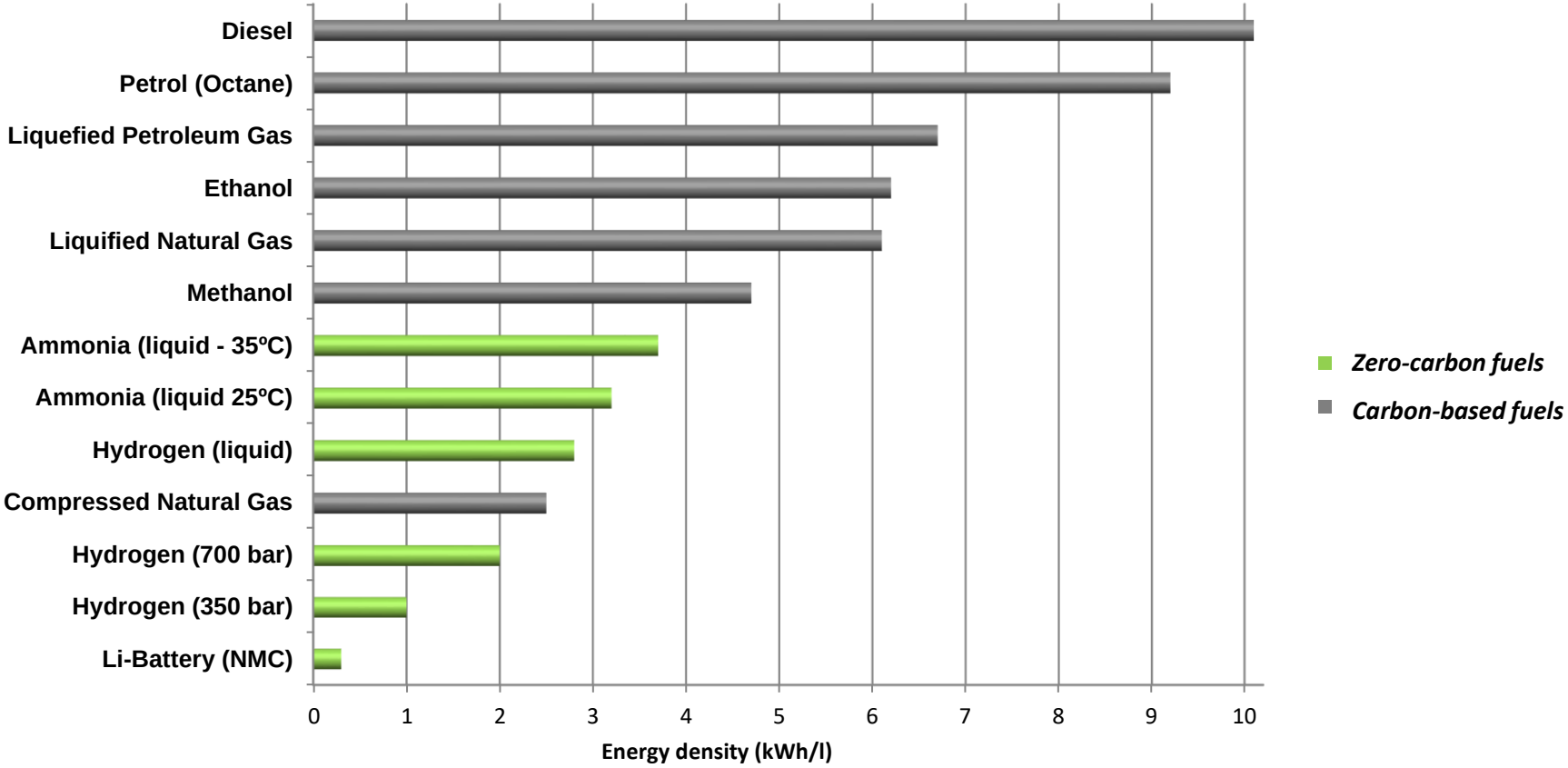
- Renewable energy is playing an important role in addressing some of the key challenges facing today's global society, such as the cost of energy, energy security and climate change.
- Energy storage is crucial for overcoming the inherent intermittency of renewable resources and increasing their share of generation capacity.
- Sustainable energy production can only work well when the specific different energy storage challenges are solved: provide the required capacity for grid-scale energy storage.
- 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.

1. Introduction

- Non battery-based storage technology, such as Power-to-X technologies (Power-to-Gas, Power-to-Chemicals, Power-to-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

1. Introduction

The volumetric energy density of a range of fuel options.



2. Objective

- The ARENHA project aims at using ammonia as a green hydrogen carrier and for that purpose it develops its main activities around the green hydrogen production, ammonia synthesis, ammonia storage and ammonia dehydrogenation.

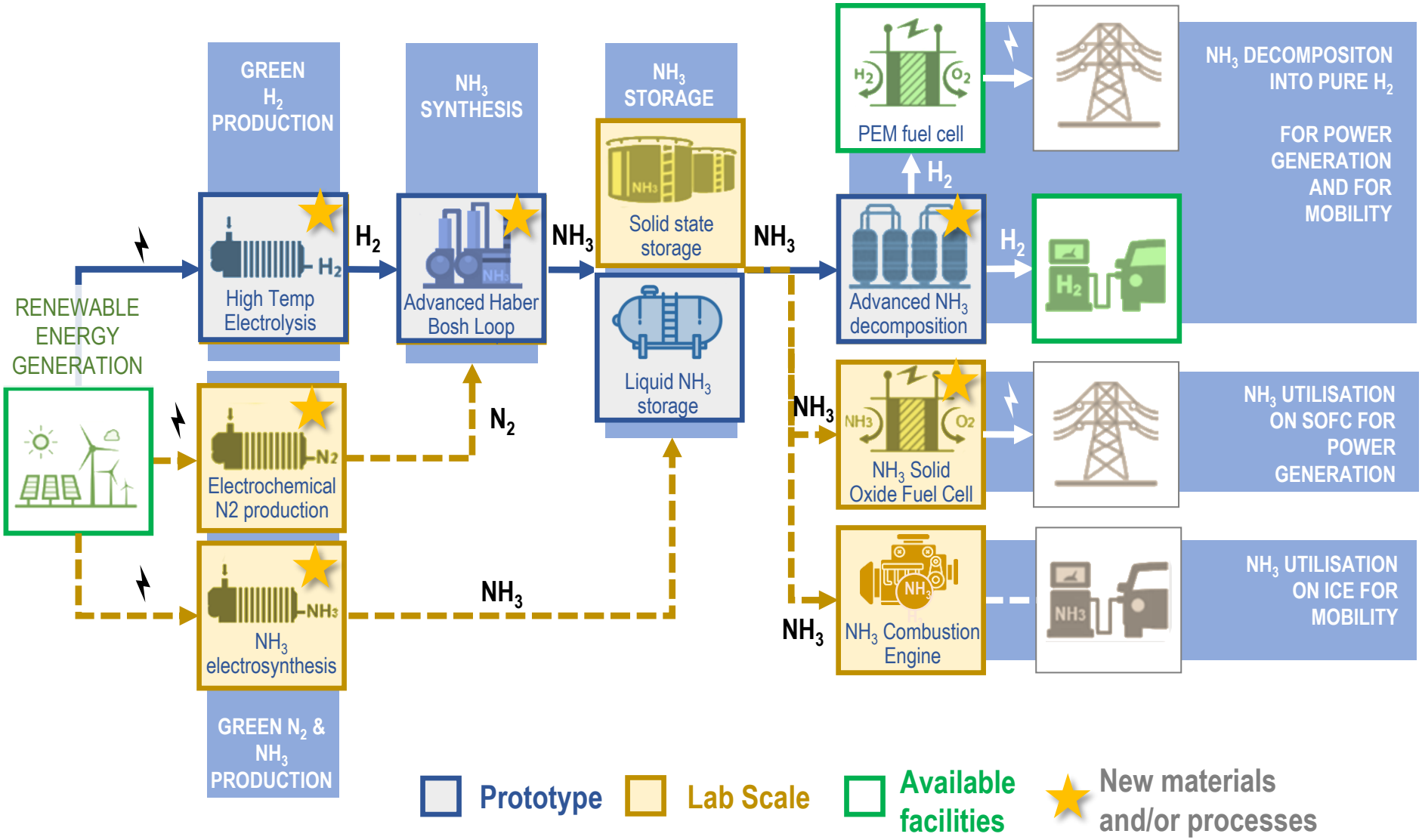
Duration: 4 years
H2020 funding 5,7 M€ approx.

- ARENHA main goal is to develop, integrate and demonstrate key material solutions enabling the flexible, secure and profitable storage and utilization of energy under form of green ammonia.

- ARENHA will demonstrate the full power-to-ammonia-to-usage value chain at TRL 5 and the outstanding potential of green ammonia to address the issue of large-scale energy storage.

2. Objective

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



3. Partnership

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

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3. Partnership

Coordination

tecnalia
MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

Universities

TU/e

DTU

Research institutions

tecnalia
MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

Centro Nacional del Hidrógeno

Fraunhofer IKTS

Science & Technology Facilities Council

Industries

PROTON VENTURES

Fuel cell technology elcogen

H2 SITE
Membrane reactors for H$_2$ generation

PSA GROUPE

ENGIE

4. Overall approach

GREEN HYDROGEN PRODUCTION

Material development and scale up

SOEC cells and stacks

Fraunhofer IKTS

elcogen

Prototype manufacturing

SOEC stack modules and BoP

Fraunhofer IKTS

elcogen

Centro Nacional de 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

Centro Nacional de Hidrógeno

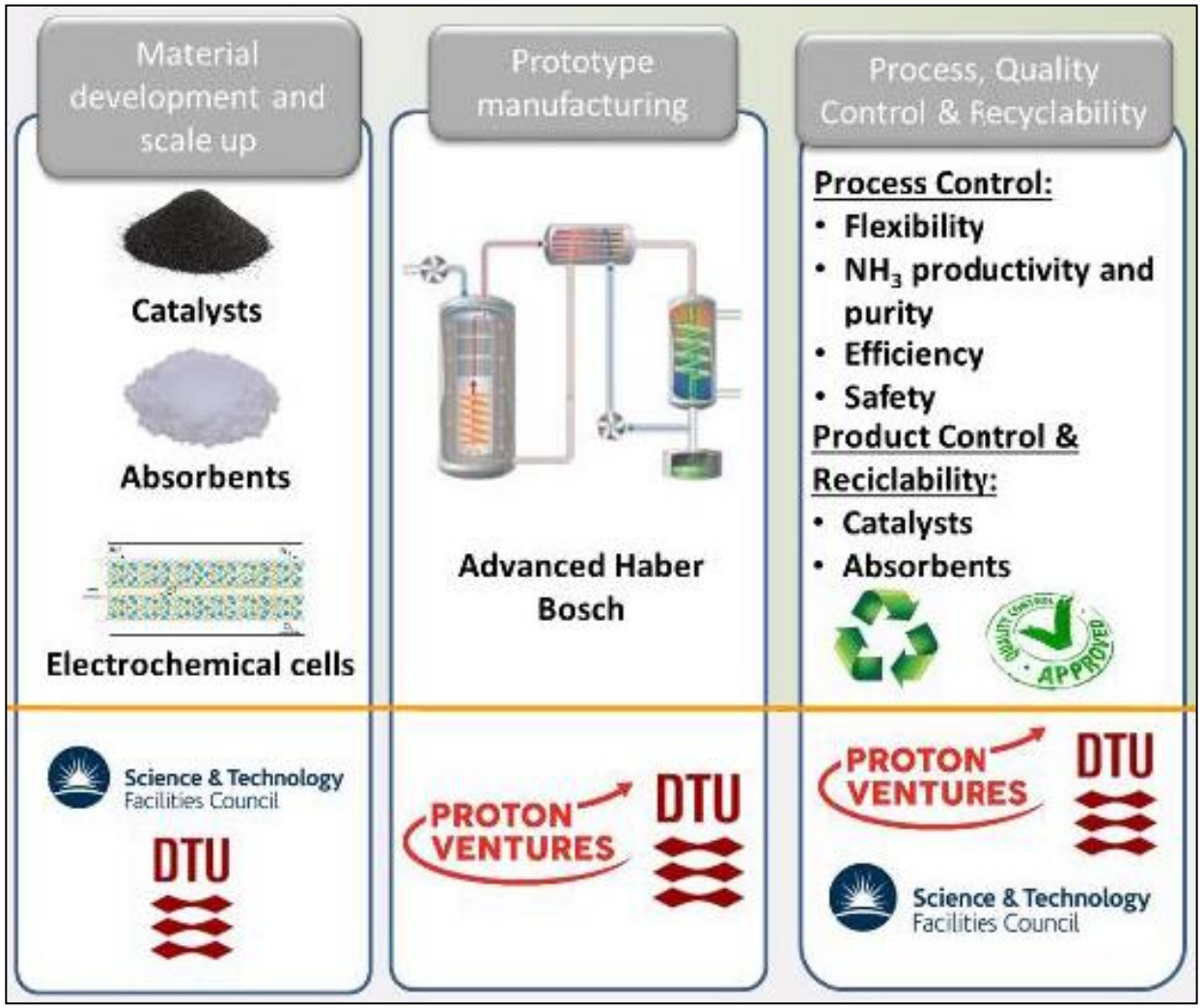
Benchmarking of novel technologies

Battolyzer

PROTON VENTURES

4. Overall approach

AMMONIA SYNTHESIS

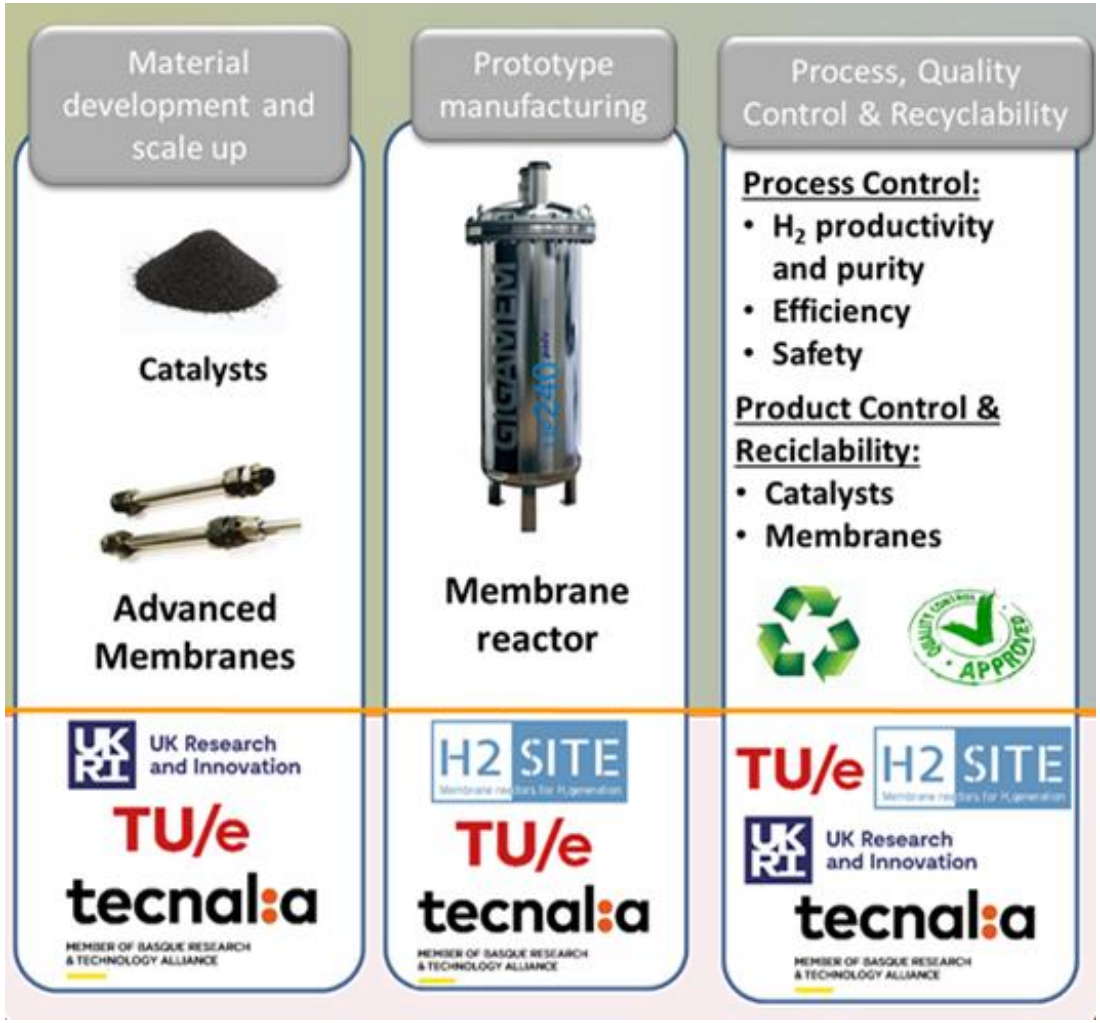


4. Overall approach

AMMONIA STORAGE

4. Overall approach

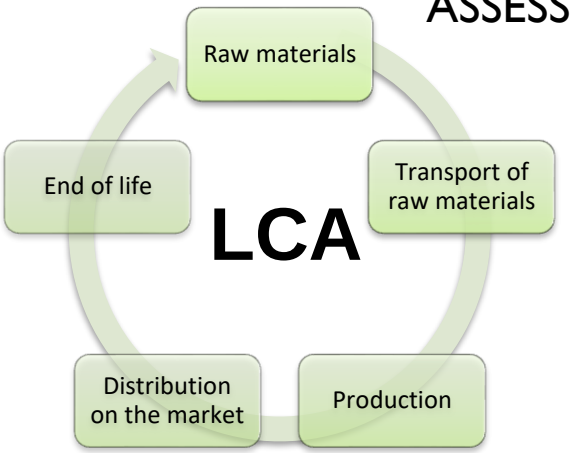
AMMONIA DECOMPOSITION

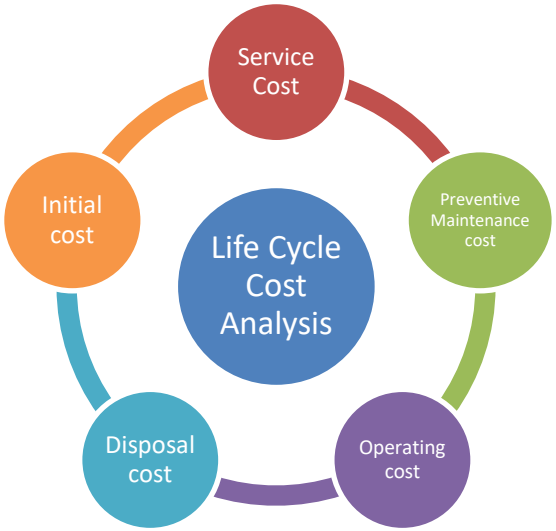


4. Overall approach

AMMONIA USAGE

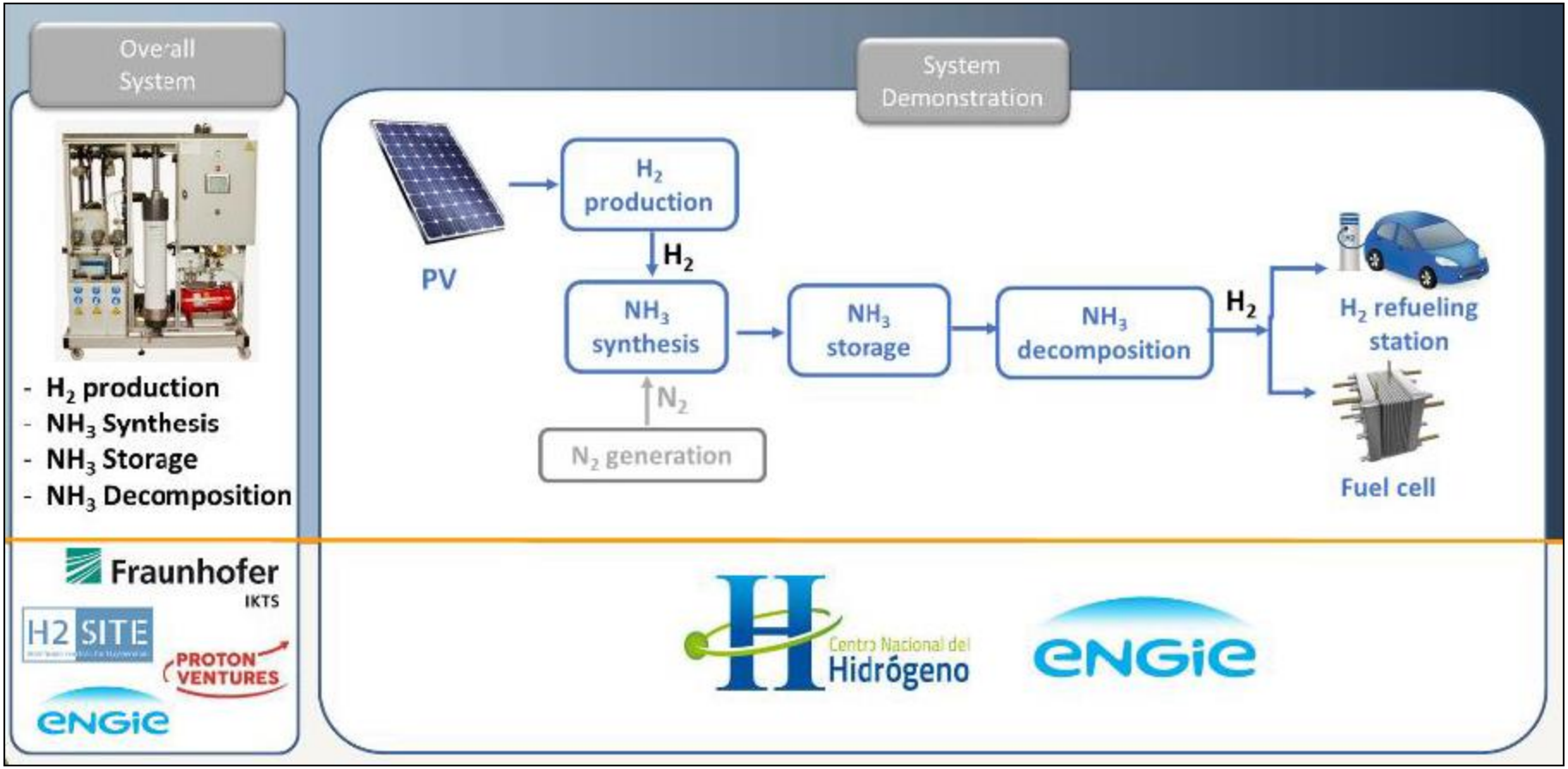
ENVIRONMENTAL LCA, ECONOMY AND SAFETY ASSESSMENT





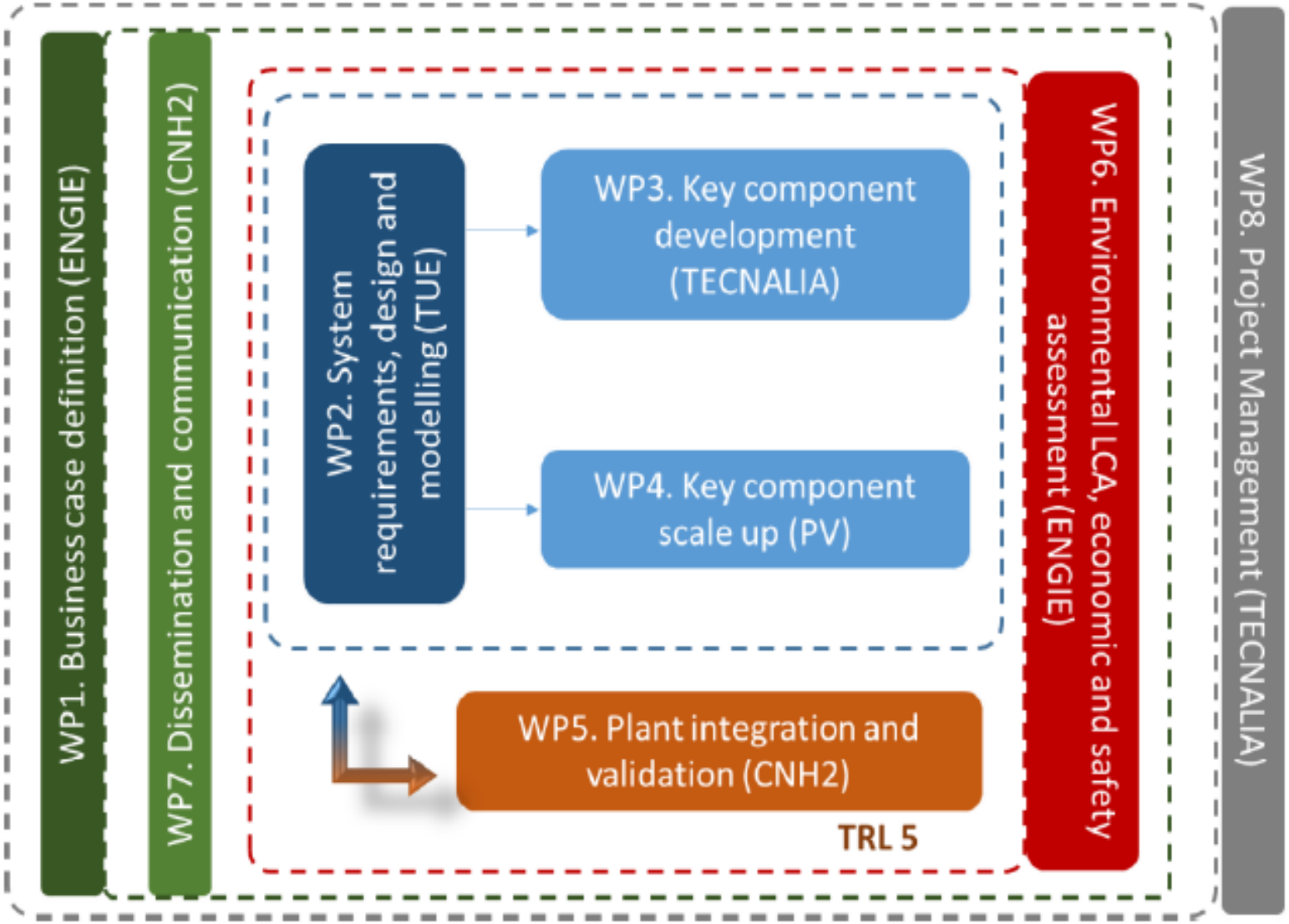
4. Overall approach

SYSTEM INTEGRATION AND DEMONSTRATION



Demonstrate the full power-to-ammonia-to-usage value chain at TRL 5.

5. Project Structure and planning



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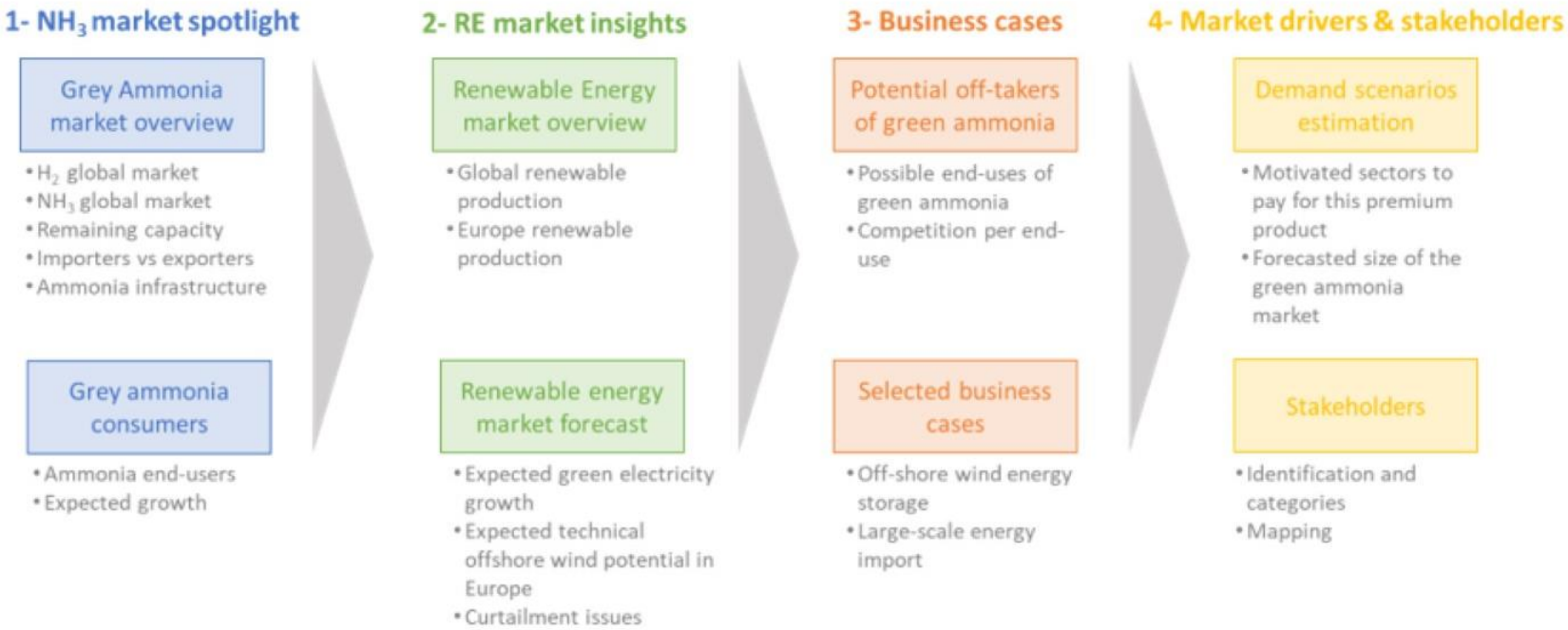
6. Progress: WP1

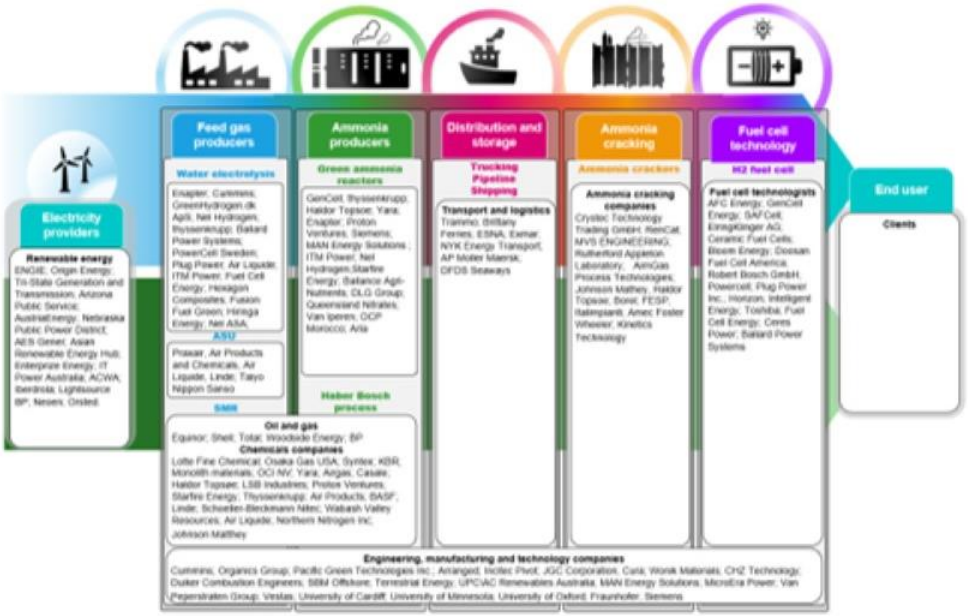
- Market and stakeholder analysis focused on the present and expected markets considering ammonia production, transport and storage.



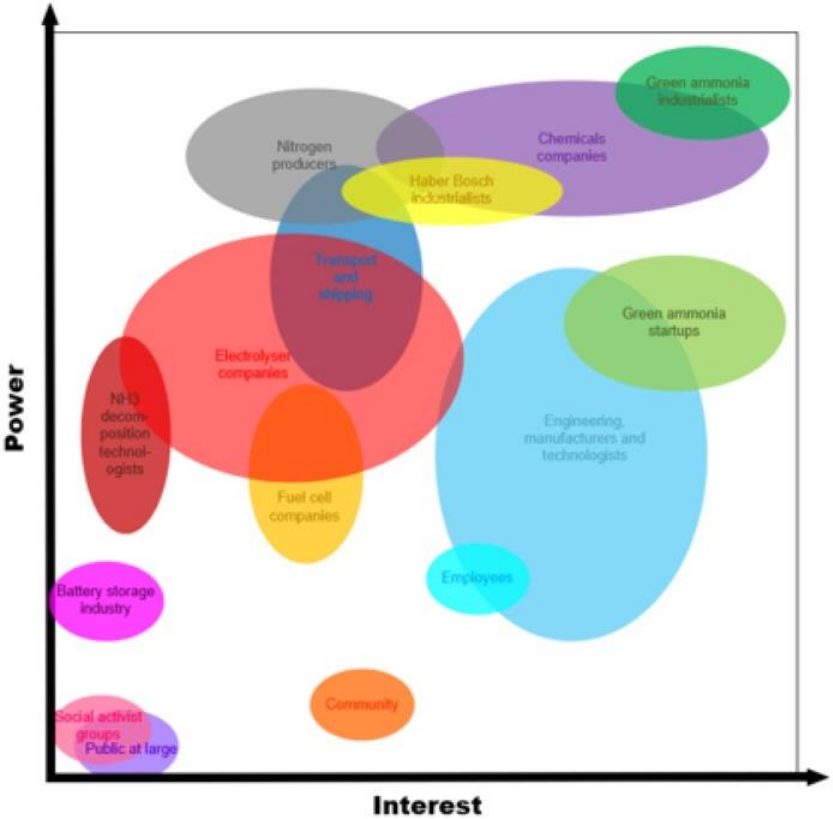
- Potential offtakes of green ammonia included the fertilizer industry, power generation, land transport sector, and maritime sector.

6. Progress: WP1

- Stakeholder mapping was carried out by estimating the power and the interest of stakeholders



Supplier stakeholder groupings along the ammonia value chain



Stakeholder mapping

- Many stakeholders belong to multiple stakeholder categories. This was mostly the case for large companies, whose activities encompass multiple stages of the ammonia value chain

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6. Progress: WP1

- Identification and assessment of the possible exploitable results develop in the frame of the ARENHA project.

Nº	Exploitable Result
1	Ammonia based energy storage system
2	Advanced Electrolyte Supported Cell SOEC electrolyser for renewable hydrogen production
3	Advanced Anode Supported Cell SOEC electrolyser for renewable hydrogen production
4	Elcogen stack module
5	Advanced ammonia synthesis unit
6	Advanced ammonia decomposition membrane reactor using DS Pd-based membranes
7	Carbon molecular sieve membranes selective to NH_3 in gas mixtures of NH_3 with H_2 and/or with N_2.
8	System to produce ultrapure hydrogen from ammonia
9	Advanced Pd-based membranes for hydrogen purification
10	Carbon molecular sieve membranes for hydrogen purification
11	Software tools (Membrane reactor design)
12	Consulting services on LCA for ammonia energy storage and supply system
13	Electrochemical N_2 production
14	Ammonia electrosynthesis
15	Ammonia solid state storage
16	Absorbent materials for ammonia synthesis (based on Haber Bosch system)
Nº	**Exploitable Result**
17	Novel catalyst for ammonia synthesis
18	Novel catalyst for ammonia decomposition
19	Recycling of Pd-based membranes
20	Ammonia SOFC, SOFC systems and system simulation for power generation
21	Ammonia combustion engine

Orange background: proposal KERs; Clear orange: original KER split in two.

6. Progress: WP2

System requirements, design and modelling

Objectives

- Define the industrial requirements for a novel integrated system for ammonia-based energy storage system including a green hydrogen production unit, an ammonia production unit and an ammonia decomposition membrane reactor together with an ammonia storage
- Material modelling for selection of the best candidates
- Reactor modelling, simulation and design
- Process simulation (process design and optimization)
- Pilot plant simulation / Modelling of the complete system
- Techno-economic assessment of the integrated plant and comparison with benchmark technologies
- Define the roadmap for future technology deployment

6. Progress: WP2

System requirements, design and modelling

The following tasks have been achieved:

- The industrial requirements for a novel integrated system ammonia-based storage energy supply system consisting of a SOEC electrolyzer, an ammonia production unit, an ammonia decomposition membrane reactor and an ammonia storage unit have been defined.
- SOEC electrolysis modelling
- Ammonia synthesis modelling
- Ammonia storage modelling
- Ammonia decomposition modelling

6. Progress: WP2

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.

6. Progress: WP2

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.
- Summarize and review current level of development in modelling SOEC systems.
- Aspen Plus SOEC model updated with experimental results (FhG-IKTS).
- A first implementation concept of the SOEC-model in Aspen Custom Modeler was developed.

- Development of a steady state SOEC system model
- Development of a dynamic state SOEC system model

6. Progress: WP2

System requirements, design and modelling

Ammonia synthesis modelling

- A dynamic model of the ammonia synthesis unit is required to optimize the reactor-catalyst synergy towards minimal losses due to pressure and temperature. The modelling will be used to translate the pilot plant results to relevant product-scale.
- Density Functional Theory (DFT) calculations and experimental characterization with Differential Electrochemical Mass Spectrometry (DEMS) were used to screen and optimize electrocatalysts for ammonia electrosynthesis
- The optimized composition of sorption materials and characterization of the absorption kinetics and thermodynamic equilibrium was determined with DFTcalculation using a genetic-algorithm (GA-DFT).
- Dynamic simulation of the fixed bed absorption and regeneration processes. The geometry and design of the bed have been optimized by performing COMSOL Multiphysics 3D simulations.
- A quasi-steady state and a dynamic ammonia synthesis process simulation were built.

6. Progress: WP2

System requirements, design and modelling

Ammonia storage modelling

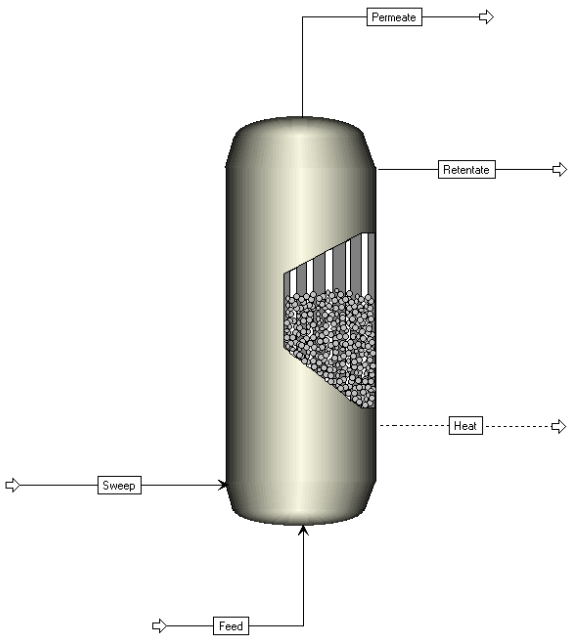
- The composition of the mixed metal halides to be synthesized for ammonia storage have been selected at DTU by performing calculations with the GA-DFT algorithm.
- The expertise and knowledge acquired from the COMSOL Multiphysics 3D simulations on the absorbent bed have been used to develop a model for the ammonia storage.
- Model validation was also performed using experimental data obtained on 10 g of sorbent.

6. Progress: WP2

System requirements, design and modelling

Ammonia decomposition modelling

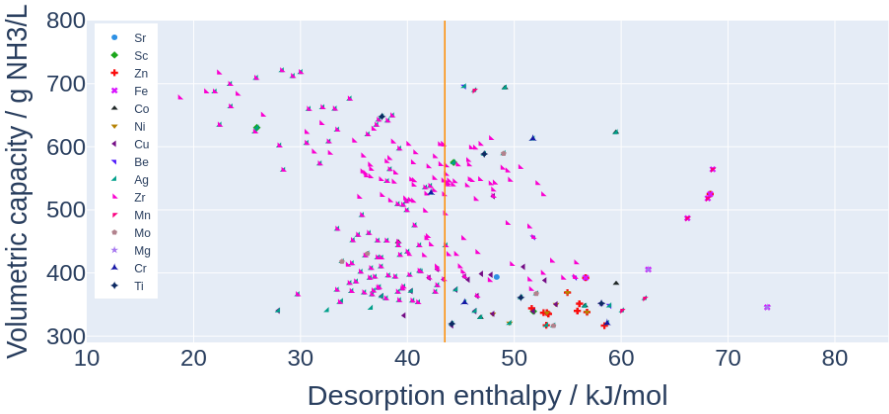
- A packed bed membrane reactor (PBMR) model for ammonia decomposition and pure hydrogen separation has been developed in ACM.



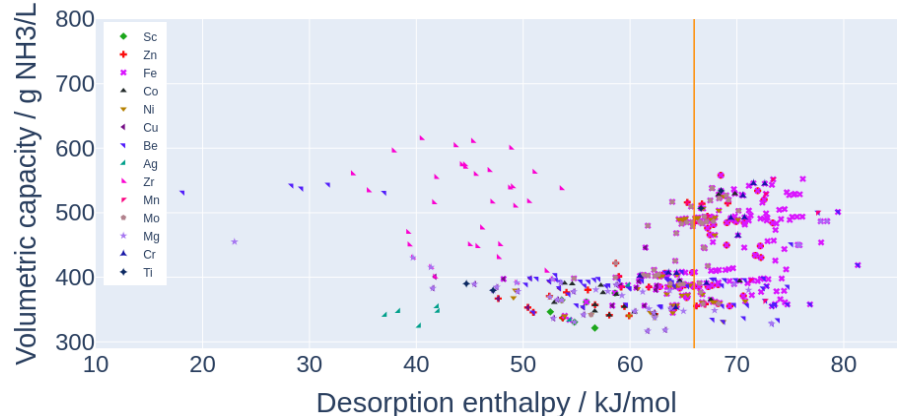
- The model was analyzed by means of a **sensitivity analysis**, showing that the model responds as expected to parameter changes.
- The model performance were **compared** to those of a model available in literature and it was concluded that the two models provide similar results
- A **validation with experimental data** obtained from lab tests was also performed and proved the model able to predict hydrogen production from ammonia decomposition with good accuracy.

6. Progress: WP2

- Genetic algorithm with density functional theory for predication of NH_3 absorption and storage were finalized. Candidate materials are selected for further experimental validation

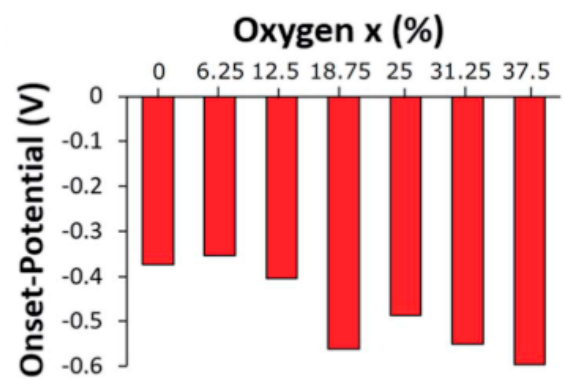


Candidate material for NH_3 storage. Targeted enthalpy: 43.5 KJ/mol

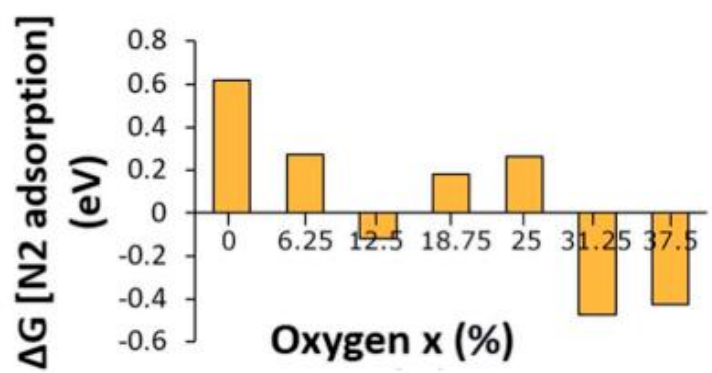


Candidate material for NH_3 absorber for HB process. Targeted enthalpy: 66 KJ/mo

- DFT calculation of electrocatalyst for NH_3 synthesis was finalized. VN mtaerials with 12% O content ($VN_{0.88}O_{0.12}$) is considered the promising candidate electrocatalyst material.



Theoretical onset potential decrease with O concentration

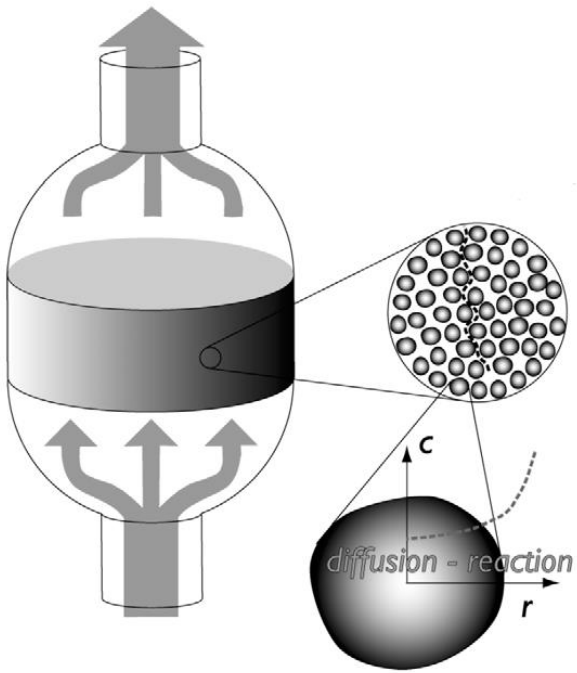


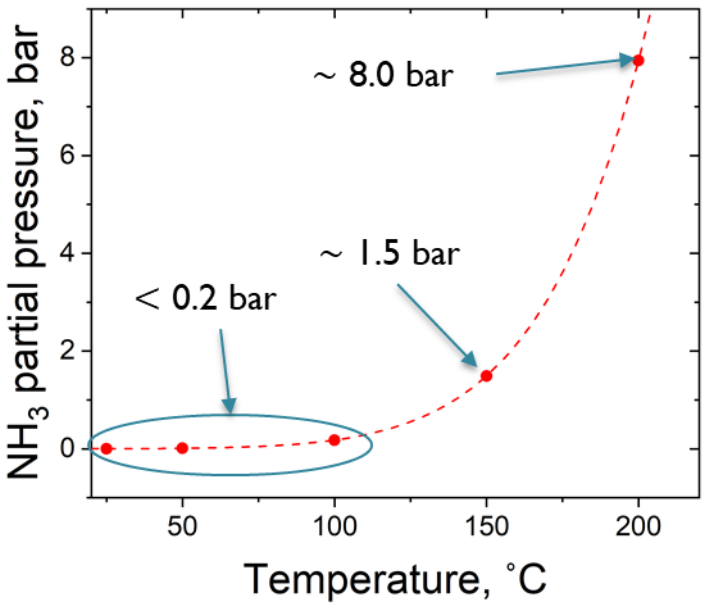
The thermodynamic barrier to N_2 adsorption decrease with O concentration

6. Progress: WP2

- COMSOL model with bi-modal porosity (macro- and microscales) were developed for modelling of absorber bed design

- Height of mass transfer zone (MTZ) and purity of outlet gas for various temperature and absorber radius



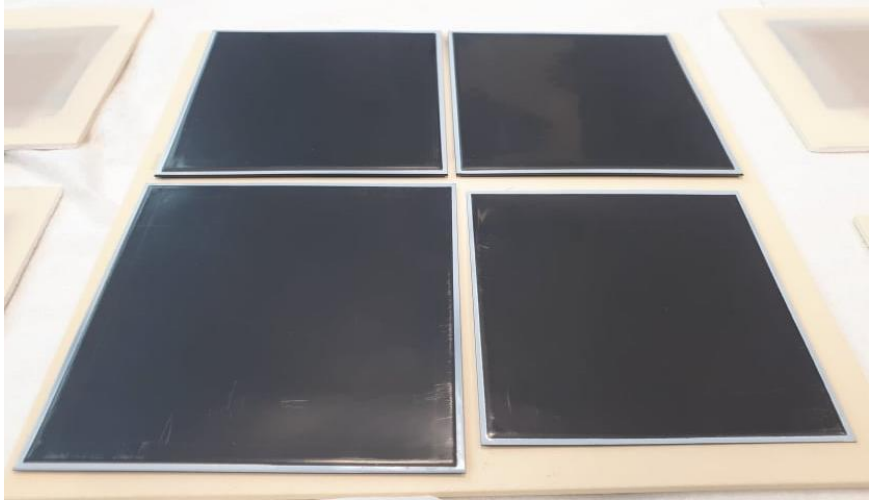


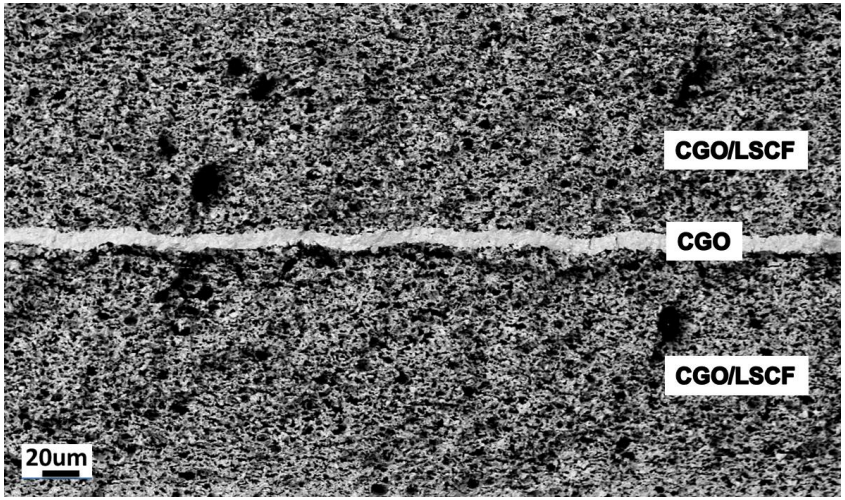
Development and characterization of modified ESCs for SOEC for H_2 production

- Development of improved cell
  - Improvement on electrode architecture
    - Promising electrode powder compositions investigated by printing on full cells and characterizing by area specific resistance (ASR) amongst others
    - Decrease of ASR of full cells by approx. 25% at 800°C compared to standard cells
  - Utilization of thinner electrolyte
    - Investigation of electrolytes with thickness < 165 µm
    - Investigation of different adhesion layers with promising results for electrolytes with a thickness of 165 µm and 110 µm
    - Decrease of ASR of full cells with 110 µm electrolyte and adhesion layer by approx. 29% at 800°C compared to standard cells
- Next step: further optimisation of cells with thinner electrolyte

6. Progress: WP3

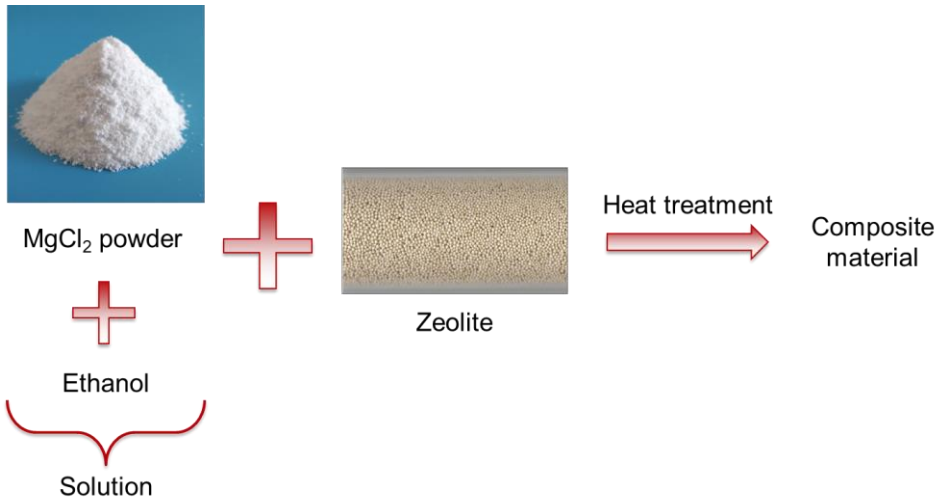
- Asymmetrical electrochemical cells with dense $Ce_{0.9}Gd_{0.1}O_{1.95}$(CGO) electrolyte and porous $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$-$Ce_{0.9}Gd_{0.1}O_{1.95}$(LSCF-CGO) composite electrolyte were successfully produced

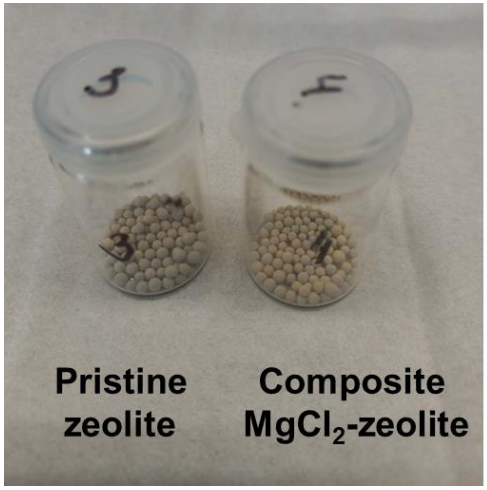




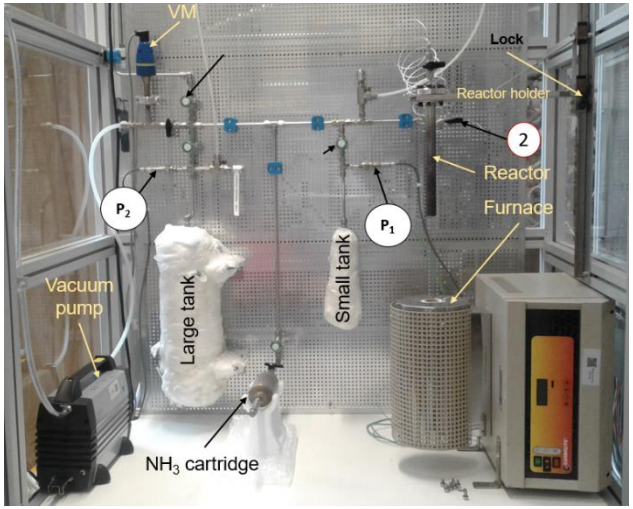
6. Progress: WP3

- Absorber materials $MgCl_2$ loaded in zeolite were produced





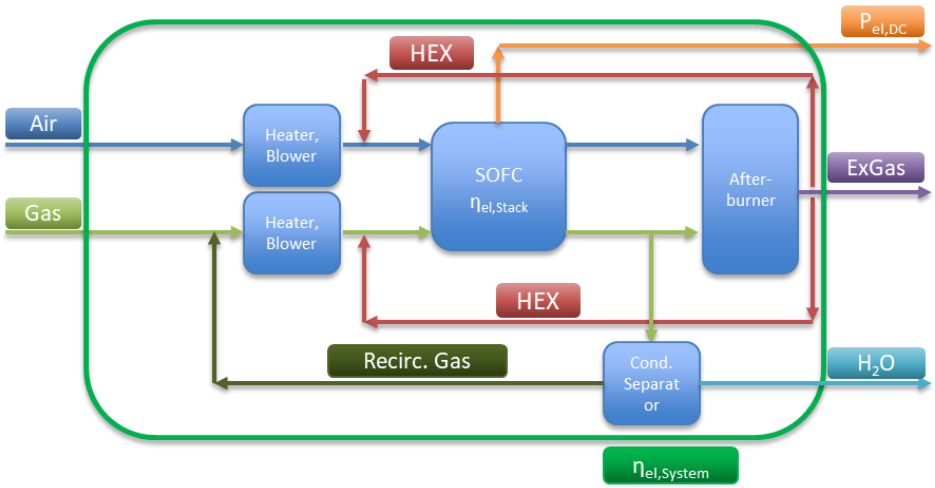
- Sieverts setup for identification of thermodynamic and kinetic parameters of absorber materials is upgraded.

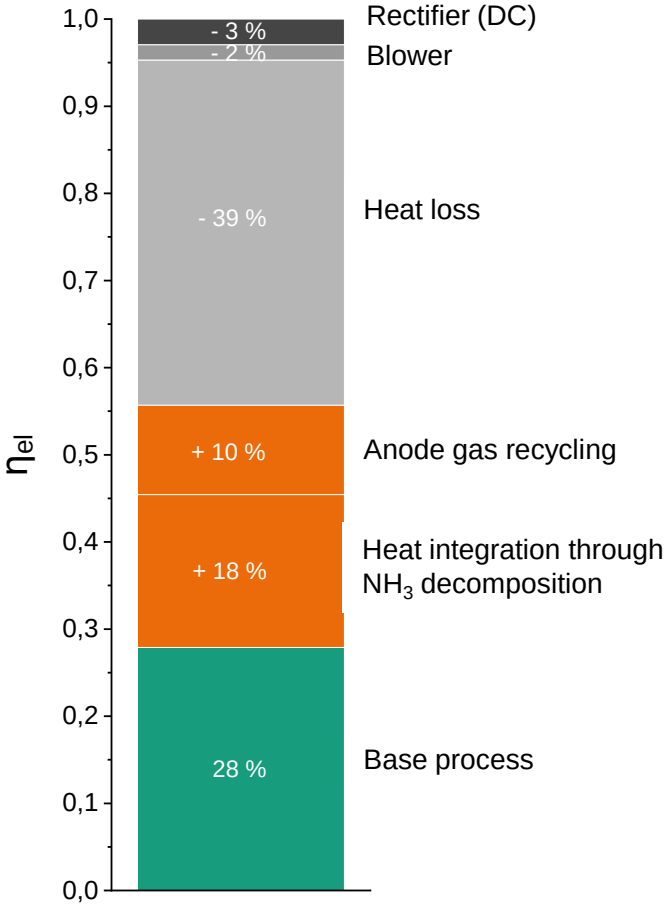


6. Progress: WP3

Characterization of SOFC system for power generation from ammonia

- Simulation of SOFC using ammonia fuel:
  - 100 % ammonia, anode gas recycling
  - System efficiency: 56 %



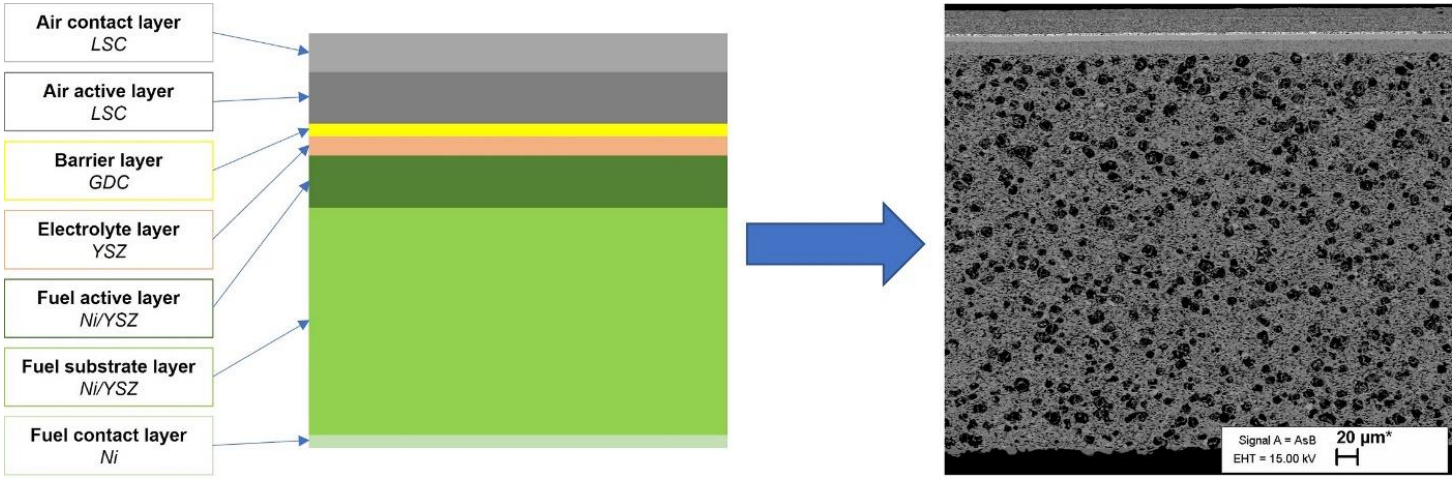


- Next step: SOFC stack tests with ammonia

6. Progress: WP3

Elcogen – Development of improved SOEC

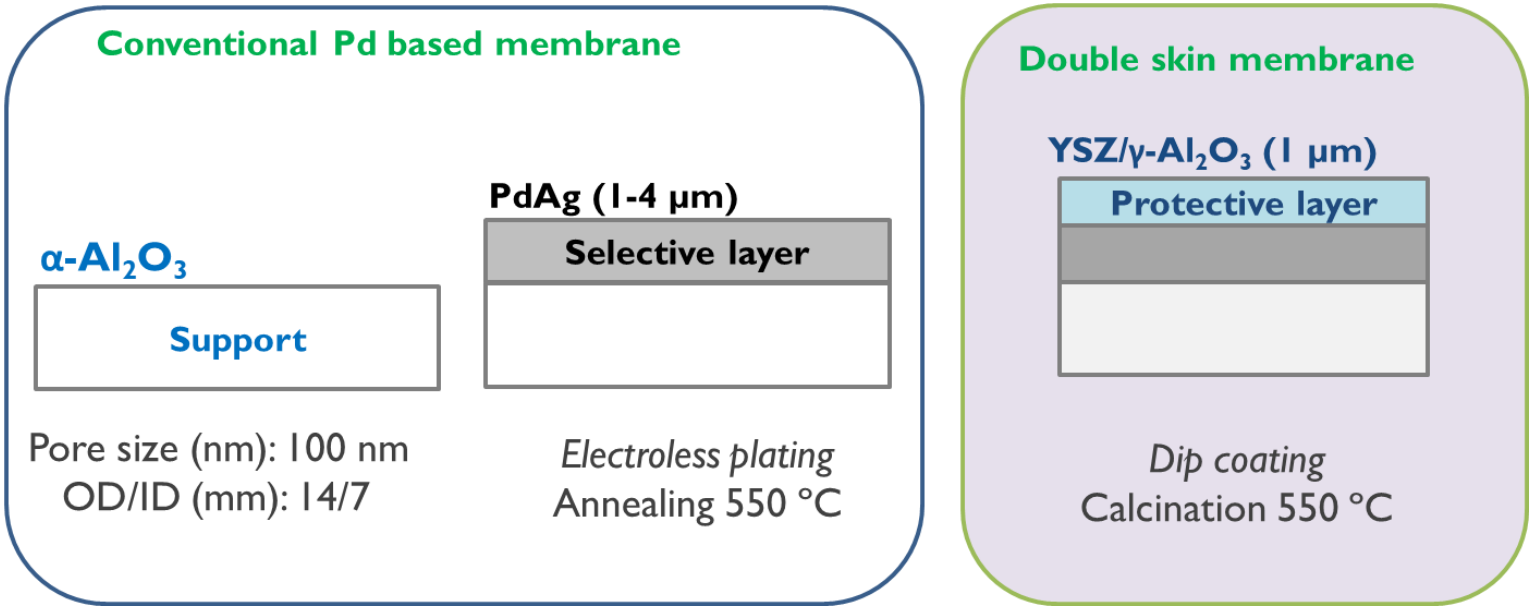
- The state-of-the-art SOFC is not optimized for electrolysis operation at high current density.
- New materials and microstructural changes in the air active layer and fuel active layer have been explored to optimise cell for SOEC mode.
- New SOECs will be manufactured incorporating all the findings 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.

6. Progress: WP3

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

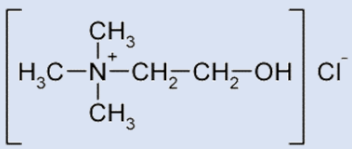
6. Progress: WP3

Recycling of Pd-based membranes

Evaluation of different DES leaching medias

Hydrogen bond acceptor

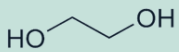
Choline Chloride



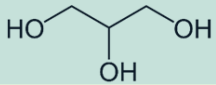
Hydrogen bond donors

Alcohols

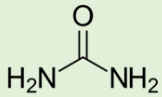
Ethylene glycol



Glycerol

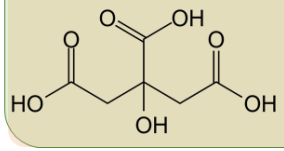


Urea

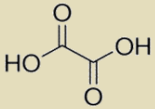


Acids

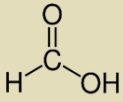
Citric acid



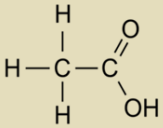
Oxalic acid

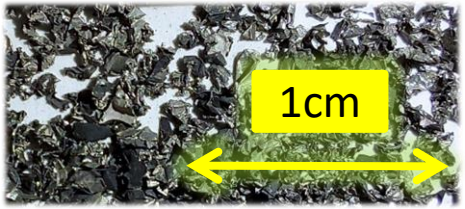


Formic acid



Acetic acid

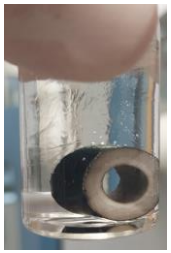




+ additives

Acid	HCl	**Chloride**	NaCl	**Oxidizing agent**	H_2O_2

>90% Pd & Ag leaching (grinded residue)



Similar recovery yield for full spent membrane

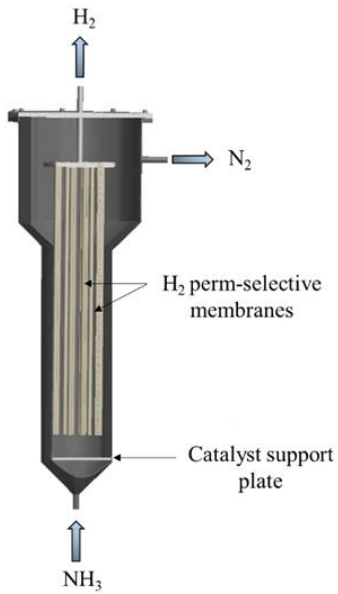
6. Progress: WP3

H_2 production via ammonia decomposition

The Pd-based **membrane reactor** is a technology with high potential to efficiently recover H_2 from NH_3

Ammonia decomposition

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

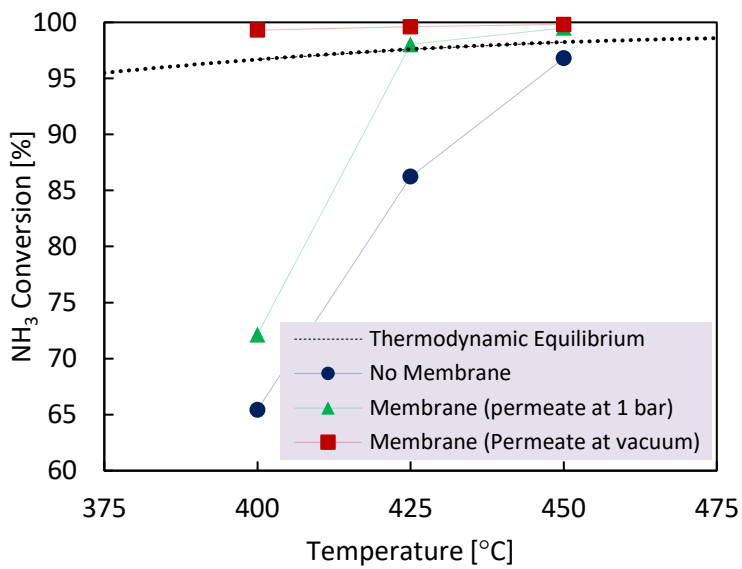


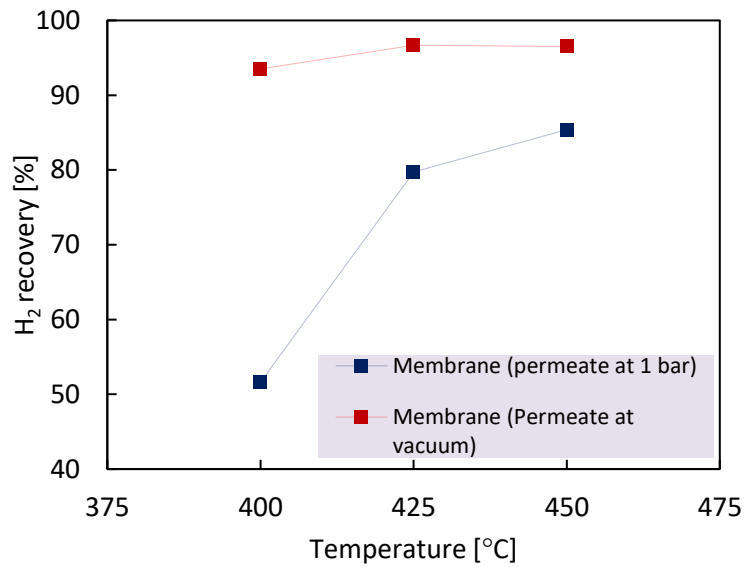
NH_3 decomposition reaction into H_2 and N_2 and high-purity H_2 separation are simultaneously performed

- the high-purity H_2 recovered through the membranes can be fed directly to FCs avoiding the need to introduce any costly separation/purification unit
- full NH_3 conversion can be achieved reducing the downstream cleaning of unconverted species
- high H_2 separation efficiencies of H_2 can be achieved at lower operating temperatures compared to conventional systems, with benefits from an energetic point of view
- since the whole process occurs in a single unit, the footprint of this technology is reduced

6. Progress: WP3

The catalytic membrane reactor for NH_3 decomposition (*)





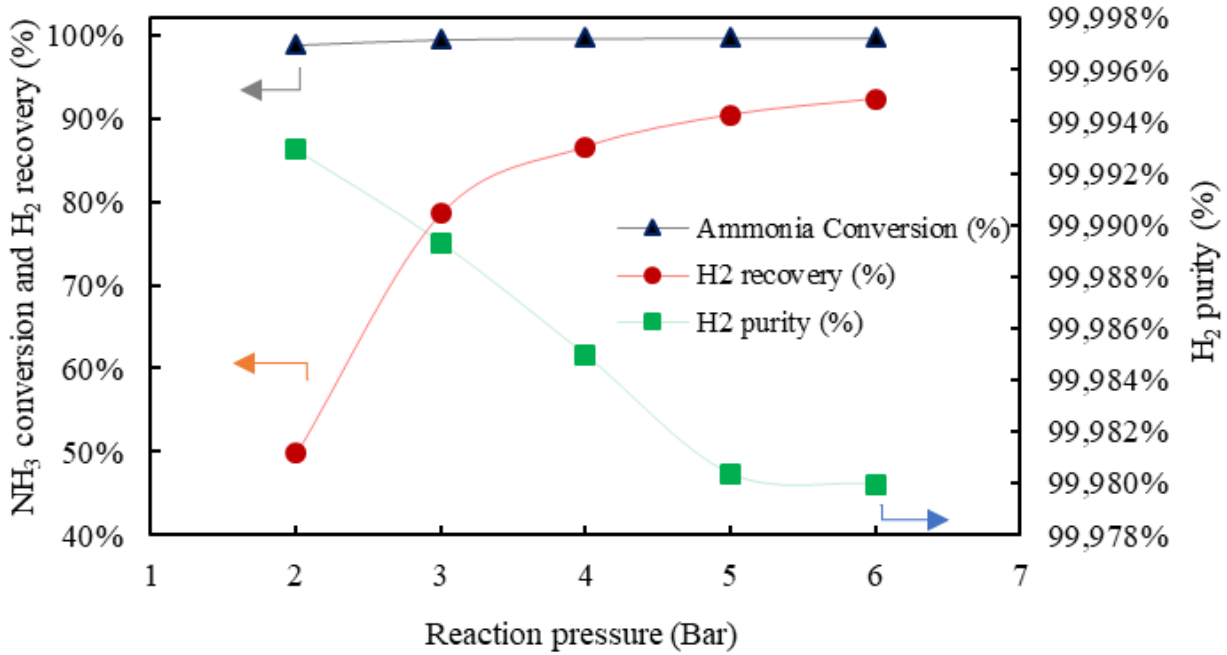
Experimental conditions	
ΔP	3 bar
Permeate pressure	0.01-1 bar
Feed flow rate	0.5 LN/min
Temp.	400, 425, 450 °C

- In a **conventional packed bed reactor**, the conversion achieved is limited, and cannot reach the thermodynamic equilibrium conversion.
- When the **membrane reactor** is adopted, the conversion is increased and for temperatures from and above 425 ◦C NH_3 conversions higher than the equilibrium without the membrane are achieved.
- The use of vacuum at the permeate side of the membrane enhances the performance of the membrane reactor technology.

(*) Valentina Cechetto et al. Fuel Processing Technology 216 (2021) 106772. https://doi.org/10.1016/j.fuproc.2021.106772

6. Progress: WP3

Effect of pressure



EXPERIMENTAL CONDITIONS
- T= 450 °C
- Feed = 0.5 L_N/min NH_3
- Pd-based membrane, dead-end configuration

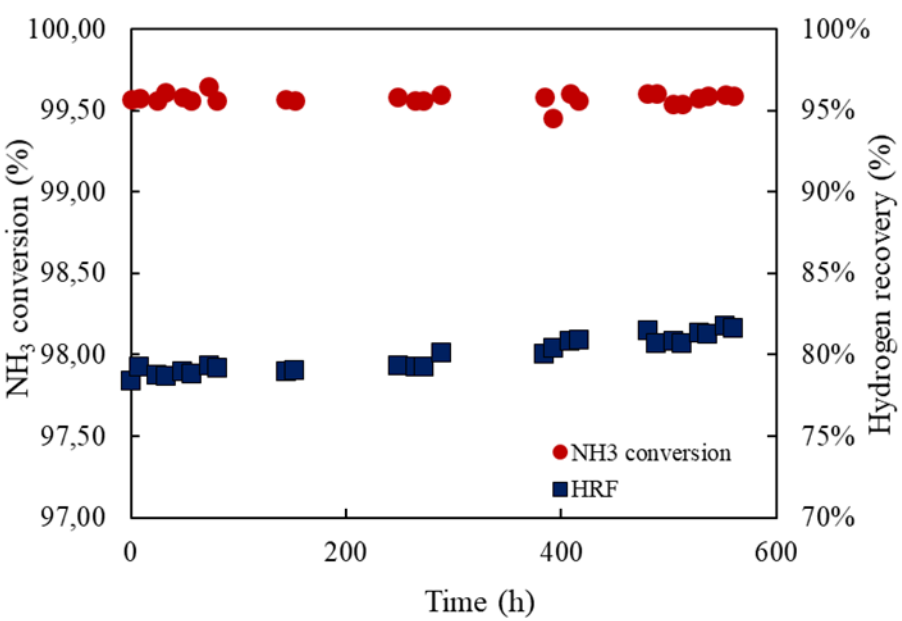
By increasing pressure in the retentate:

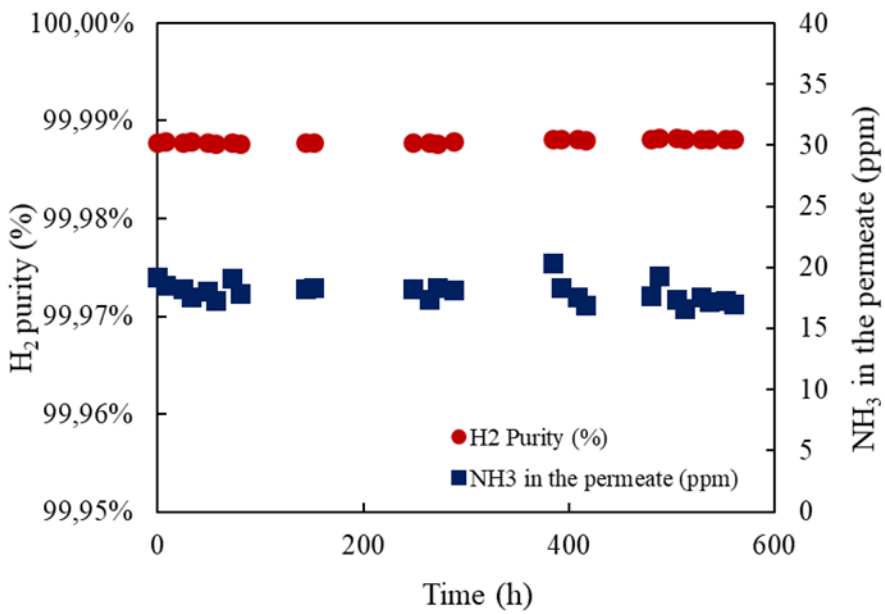
- H_2 recovery increases. Values above 90% are achieved for operating pressures higher than 5 bar.
- H_2 purity in the permeate decreases.

(*) Valentina Cechetto et al. Fuel Processing Technology 216 (2021) 106772. https://doi.org/10.1016/j.fuproc.2021.106772

6. Progress: WP3

Long term ammonia decomposition test in the membrane reactor (*)



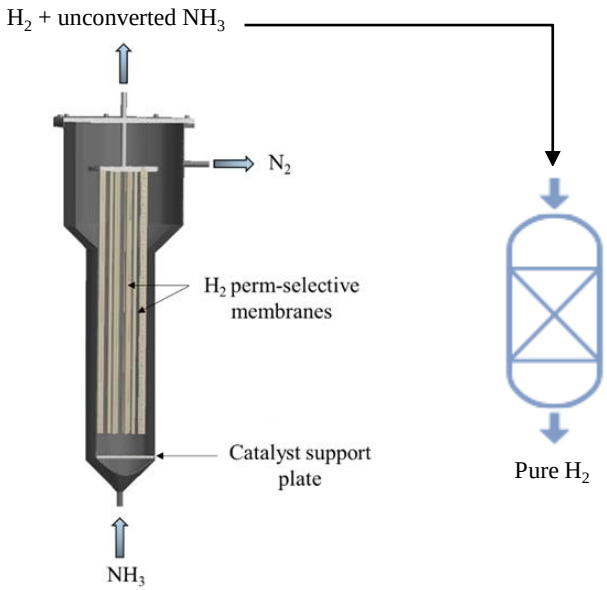


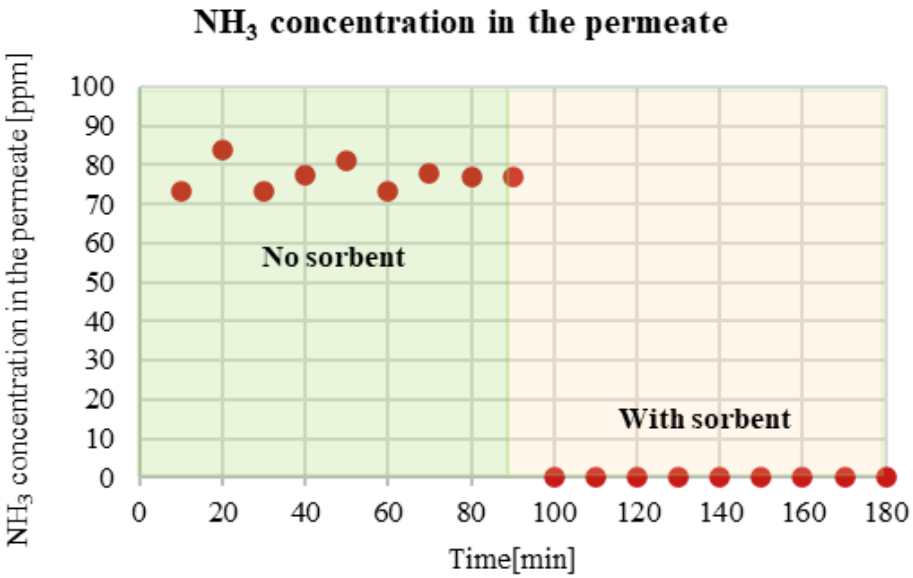
Experimental conditions: T= 450 °C, $P_{retentate}$= 3 bar, $P_{permeate}$= atmospheric, Feed= 0.5 L_N/min NH_3

(*) Valentina Cechetto et al. Fuel Processing Technology 216 (2021) 106772. https://doi.org/10.1016/j.fuproc.2021.106772

6. Progress: WP3

Addition of a H_2 purification stage





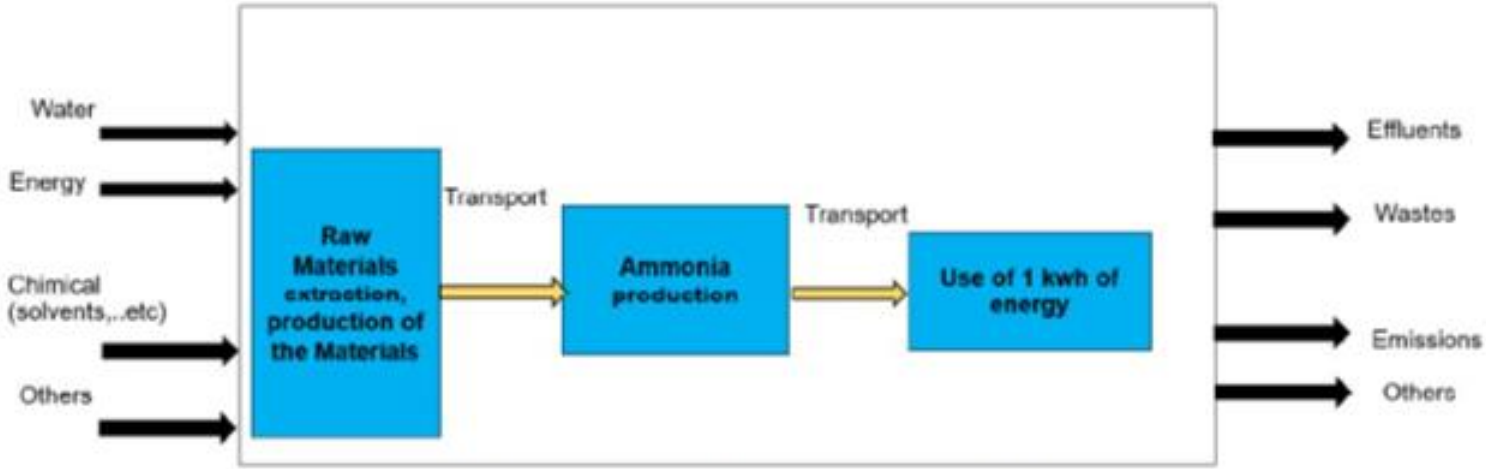
Experimental conditions: T= 400 °C, $P_{retentate}$= 3 bar, $P_{permeate}$= 1 bar, Feed flow rate = 2 L_N/min NH_3, Feed composition: 5% NH_3 and 95% H_2

- In order to purify H_2 from unreacted ammonia produced during dehydrogenation reactor, a H_2 purification stage on the permeate side of the membrane was added.
- A commercial **zeolite 13X** was tested as adsorbent material.

(*) Valentina Cechetto et al. World Online Conference on Sustainable technologies. March 17-19, 2021.

6. Progress: WP6

- Goal and scope of the sociological survey and environmental LCA, LCC and LCS



LCA boundaries. Functional unit 1 KWh

- Data collected by CNH2
- Preliminary LCA running on Simapro on going by ENGIE in order to identify most significant environmental impacts and sensitive parameters
- Detailed environmental will be performed at the end of the project in order to provide a complete LCA of the processes developed in the AREHNA

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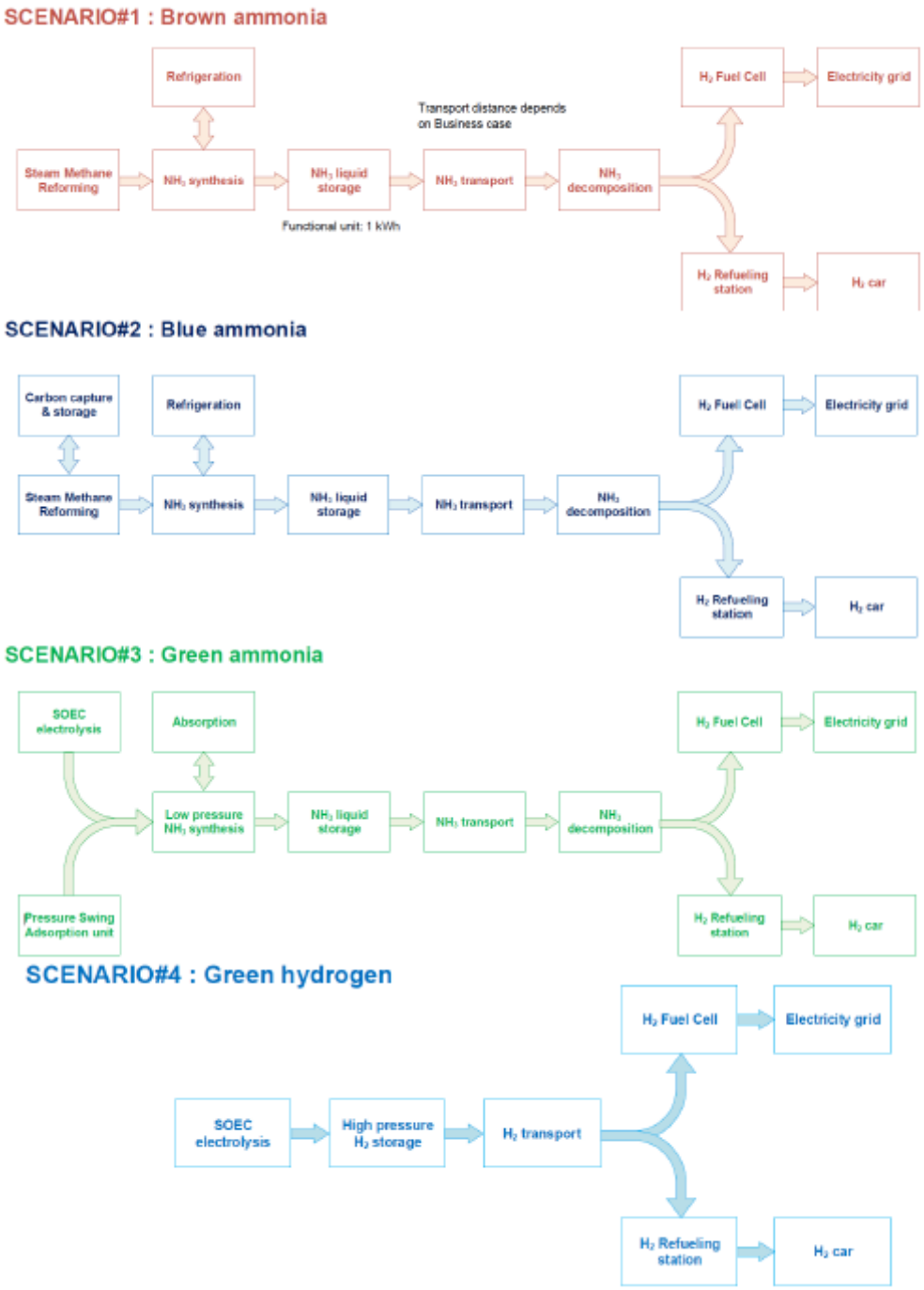
6. Progress: WP6

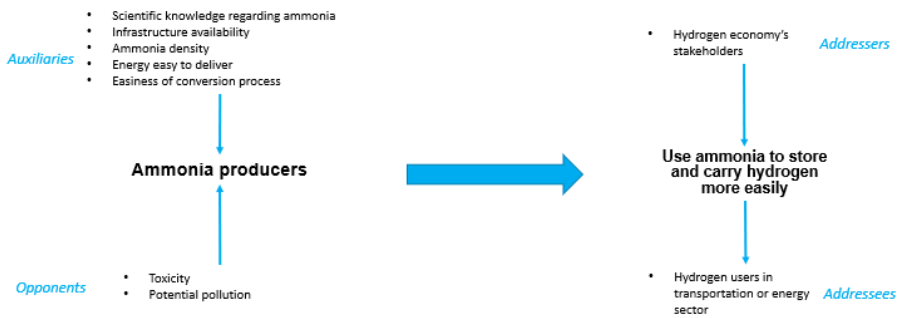
- 4 Scenarios to be studied: green, blue and brown ammonia and green hydrogen
- Literature review on going



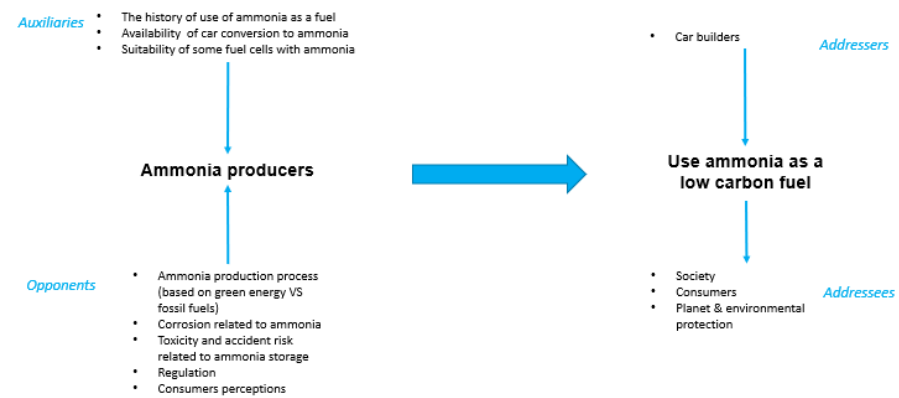
6. Progress: WP6

Social Acceptance task :
Identification of various narratives related to Ammonia

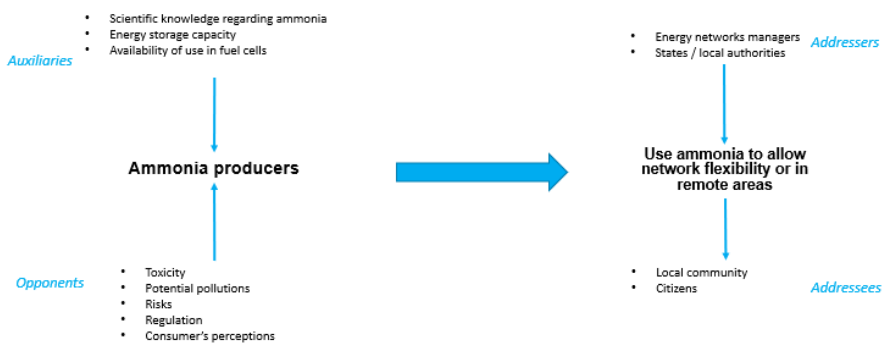
Narrative regarding ammonia as a H_2 carrier



Narrative regarding ammonia as a new fuel



Narrative regarding ammonia stationary application



- Main narratives related to Ammonia where first identified in literature
- A deeper exploration through interview was engaged
- Next steps :
  - Continue exploration through interviews in shipping sector
  - Design & pass a questionnaire to test opinion on theses narratives

6. Progress: WP7

- Project logo and set of public document templates
- Public Project website: [Home | ARENHA]
- Dissemination and Communication Plan updated M3
- Dissemination and Communication Plan updated M12
- First Public Presentation
- 6 months periodic Project newsletter M6, M12 and M18
- ARENHA First dissemination video
- ARENHA dissemination activities ongoing

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7. Impact

Decrease energy import dependency.

Promote the integration of offshore renewables for energy dependency.

Integration of renewable in power systems with large scale energy storage.

Strategic European leadership in energy storage.

Ammonia to diversify energy supply from third countries

Alternative energy import through renewable electricity storage and long distance transportation.

-  > $2.5 trillion per year
-  > 5000 future jobs
- Reduction of NOx-emission = Increase quality of life
- Avoid 20 million barrels of oil per day

Advanced materials and Reactors for Energy storage tHrough Ammonia

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Thank you for your attention

Website: arenha.eu/
LinkedIn: ARENHA Project
Twitter: @ARENHA_H2020