112CO2

Low temperature catalytic methane decomposition for COx-free hydrogen production

European Hydrogen Week

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#PRD2021
#CleanHydrogen

FCH

European Commission

Project Overview

- Call year: 2019
- Call topic: FETPROACT-EIC-05-2019 - FET Proactive: emerging paradigms and communities
- Grant No.: 952219
- Project dates: 01/09/2020 – 29/02/2024
- % stage of implementation 01/11/2019: *ca.* 33 %
- Total project budget: *ca.* 3.6 M€
- 7 Partners: UPORTO (PT), CSIC (SP), DLR (DE), EPFL (CH), Quantis (CH), Paul Wurth (LU), Pixel Voltaic Lda (PT)

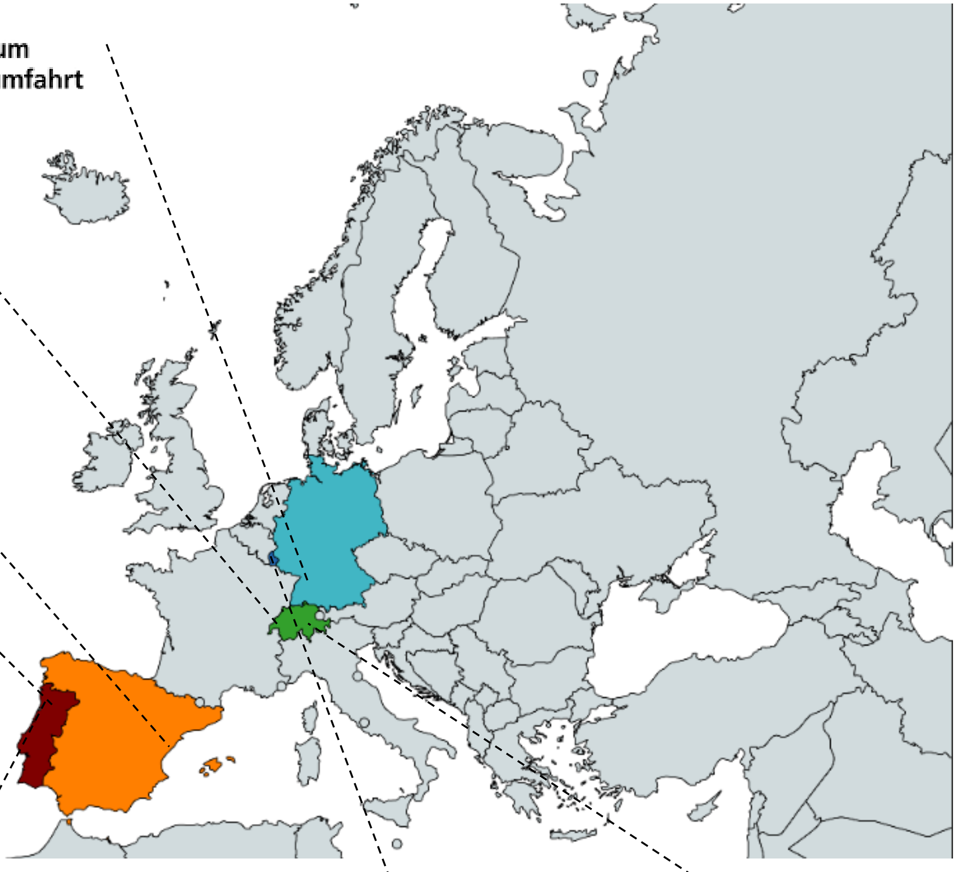
Partners

DLR Deutsches Zentrum für Luft- und Raumfahrt

EPFL

CSIC
Consejo Superior de Investigaciones Científicas
ITQ Instituto de Tecnología Química
Excelencia Severo Ochoa
Universitat Politècnica de València

U.PORTO
FEUP Faculdade de Engenharia Universidade do Porto
FLUP Faculdade de Letras Universidade do Porto



PIXEL VOLTAIC

PAUL WURTH

Quantis

Project Structure

Management

Project management and quality assurance (WP1)
Leader: UPORTO
Contributors: all partners

RTD

Development of regenerable catalysts for MD (WP2)
Leader: CSIC
Contributors: all partners

Development of PCC for hydrogen electrochemical pumping (WP3)
Leader: DLR
Contributors: all partners

Reactor design and optimization (WP4)
Leader: UPORTO
Contributors: all partners

Environmental and economic sustainability (WP6)
Leader: QTIS
Contributors: all partners

Demonstration

System integration and demonstration (WP5)
Leader: PV
Contributors: all partners

Project dissemination, exploitation and communication (WP7)
Leader: EPFL
Contributors: all partners

Framing the challenge

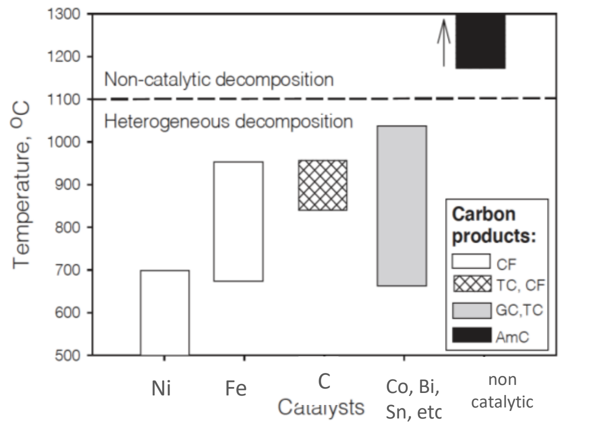
State-of-the-art

Low temperature Methane Decomposition reaction, also known as **methane pyrolysis:**

$$CH_4 \rightarrow C\ (s) + 2H_2 \qquad \Delta H^0 = 75.3\ kJ\ mol^{-1} \qquad (1)$$

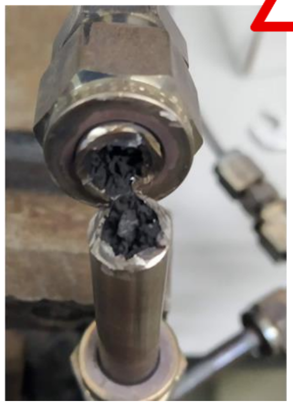
100 % selective reaction, no side-products!!

- It allows the conversion of methane to **clean H_2** and **solid carbon** from:
  - Natural gas; → Turquoise H_2
  - Biomethane (biogas); → Bright H_2
  - Synthetic methane.



N. Z. Muradov, T. N . Veziroglu, International Journal of Hydrogen Energy, 30 (2005) 225-237.

Carbon Clogging



- ***catalyst deactivates***
- ***reactor shuts-down***

State-of-the-art

Low temperature Methane Decomposition reaction, also known as **methane pyrolysis**:

$$CH_4 \rightarrow C\ (s) + 2H_2 \qquad \Delta H^0 = 75.3\ \text{kJ mol}^{-1} \qquad (1)$$

- Hydrogen production:
  - **Zero CO_x emissions**;
  - **Cost-competitive**;
  - Use the present infrastructure for natural gas;
  - **Centralized or On-site/On-board production**;
  - Can remove atmospheric CO_2 at competitive prices;
  - The development and implementation is very quick;
  - Valorization of the carbon materials: Structural materials | Power Generation | Soil Amendment | Environmental Remediation | nano-technology

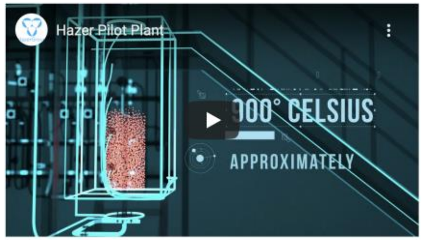
Competitors

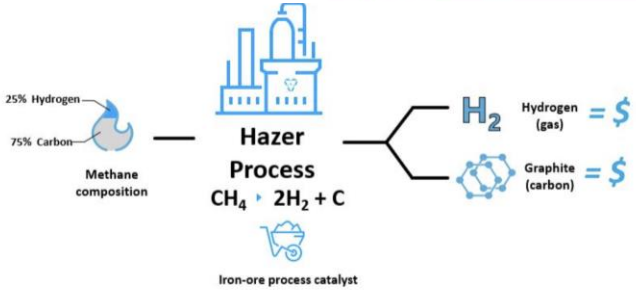
...have been pursuing methane decomposition at very (too) high temperatures!!!

HazerGroup
Local Technology for Global Markets

HAZER uses a fluidized-bed reactor loaded with iron-ore and runs at *ca*. **900 °C** to catalyze the Methane Decomposition reaction. The carbon/graphite is recovered from the iron-ore catalytic particles.

The HAZER® Process enables the effective conversion of natural gas, and similar feedstocks, into hydrogen and high quality graphite, using iron ore as a process catalyst. The aim of the HAZER® Process will be to achieve savings for the hydrogen producer, as well as providing 'clean' hydrogen with significant lower carbon dioxide emissions, enabling such hydrogen to be used in a range of developing 'clean energy' applications, as well as in large existing chemical processing industries.

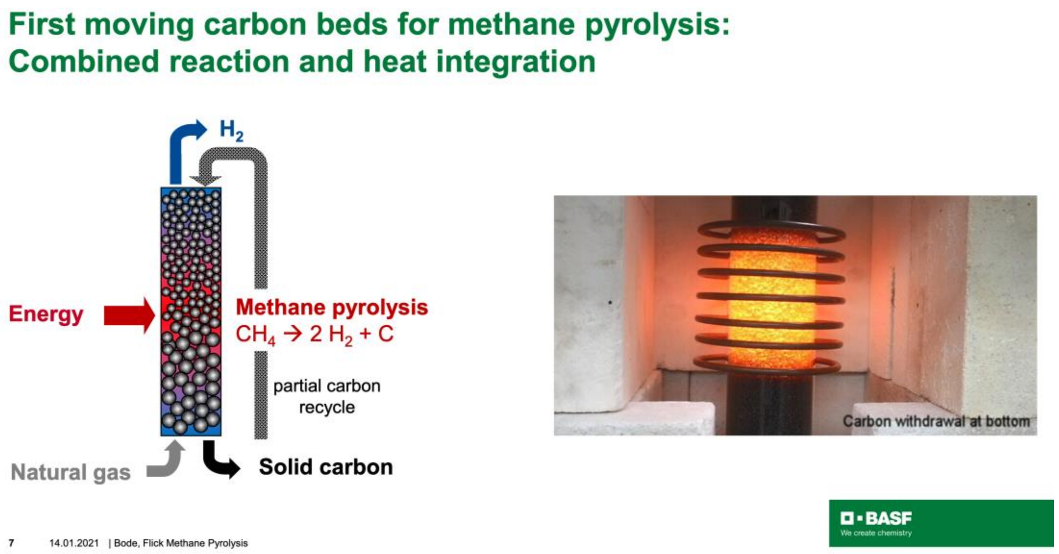




https://hazergroup.com.au/about/#hazerprocess

BASF
We create chemistry

BASF developed a moving bed reactor loaded with coal pellets, running at *ca*. **1200 °C**, which, apart from being too **energy-intensive**, also displays very **low catalytic activity**.



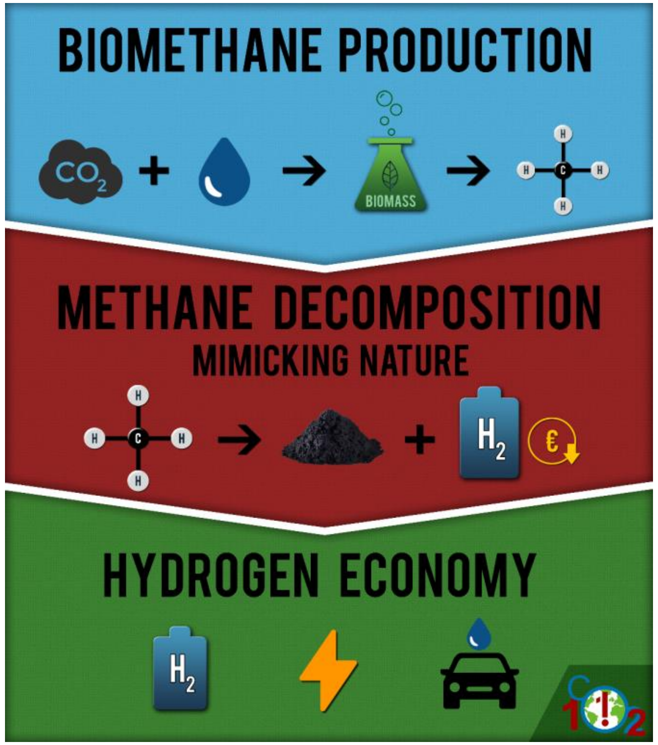
T. Marquardt, A. Bode, and S. Kabelac, "Hydrogen production by methane decomposition: Analysis of thermodynamic carbon properties and process evaluation," *Energy Convers. Manag.*, vol. 221, p. 113125, Oct. 2020.

Low temperature catalytic methane decomposition for COx-free hydrogen production

OUR TARGETS

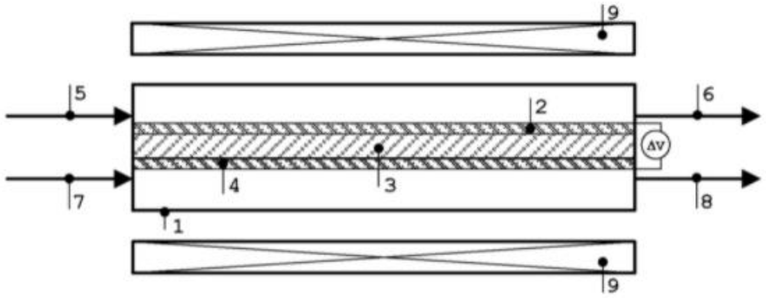
Project Summary

- Disruptive **low temperature methane decomposition** process, **at (*ca*. 550 °C),** using abundant and cheap metallic catalysts that are **cyclically regenerated**.



- The original idea was disclosed in a **patent application (WO/2020/121287) by partner Pixel Voltaic**, a spinoff of UPORTO.

1. WO2020121287 - CATALYTIC METHANE DECOMPOSITION AND CATALYST REGENERATION, METHODS AND USES THEREOF



PIXEL VOLTAIC

Project Summary

- 112CO2 goes beyond the SoA in critical areas:

1
Catalyst
tuning metal-support interaction, size-controlled synthesis, engineered catalyst

2
Proton conducting ceramics (PCC)
cost-competitive system for H_2 electrochemical purification

3
Reactor
new, extremely compact and stable reactor for conducting the MD reaction with catalytic regeneration

4
Prototype/ Pilot Station
system integration and demonstration

Project Progress/Actions - Aspects

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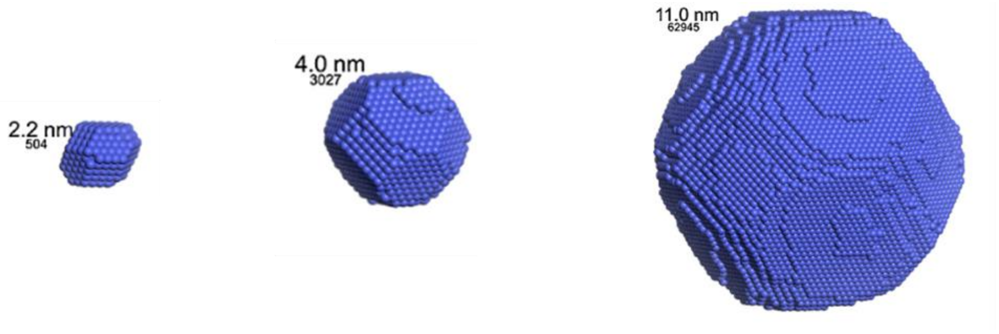
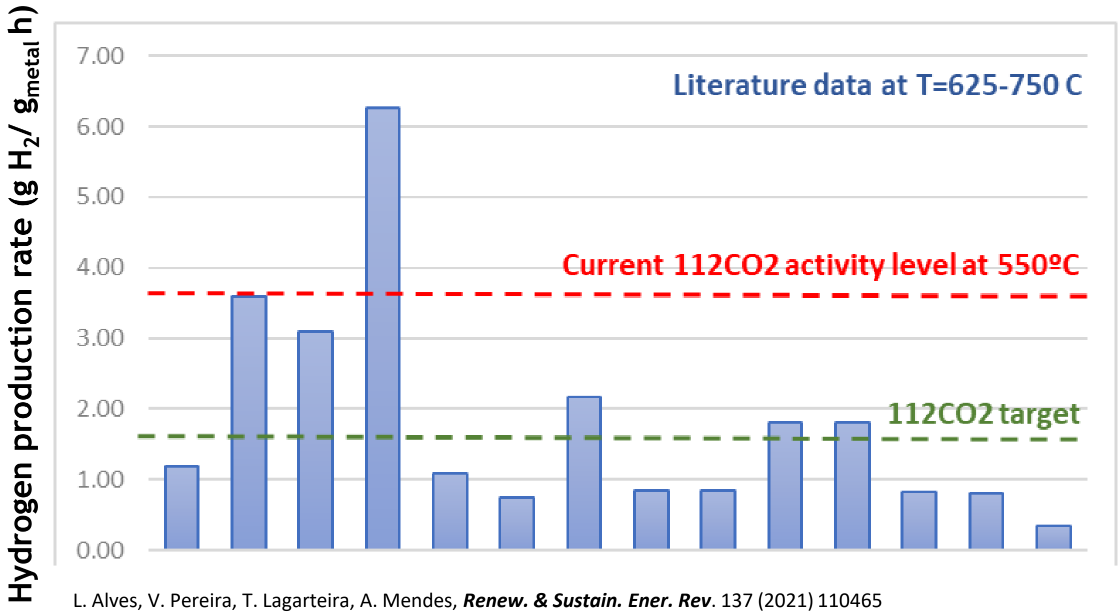
1 Catalyst WP2

MD catalyst displaying high activity and long-term stability

25% 50% 75%

$0.45\ g_{H2} \cdot g_{Cat}^{-1} \cdot h^{-1}$ H_2 production rate





L. Alves, V. Pereira, T. Lagarteira, A. Mendes, ***Renew. & Sustain. Ener. Rev***. 137 (2021) 110465

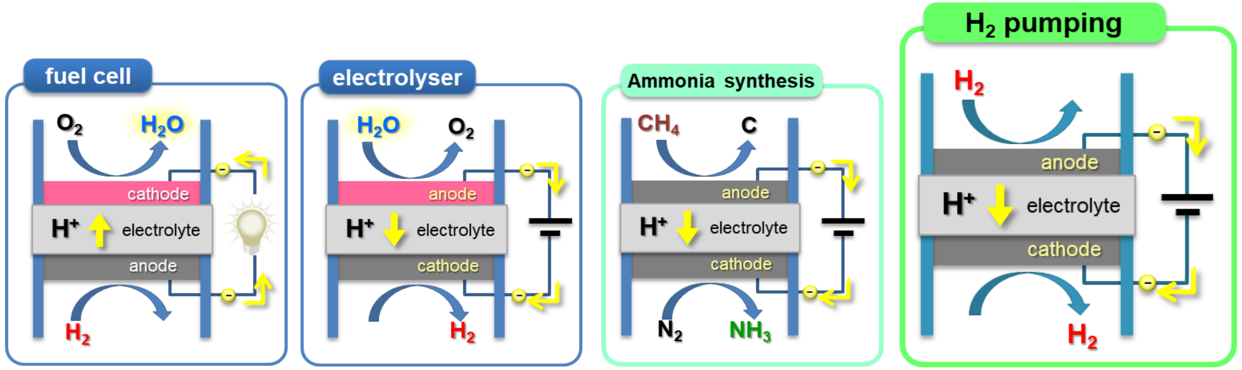
Project Progress/Actions - Aspects

2 Proton conducting ceramics (PCC)

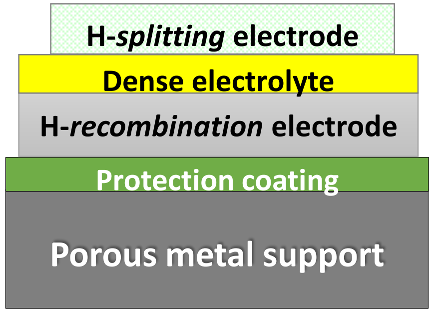
WP3

Proton conducting ceramics (PCC) for efficient and cost-effective H_2 purification, working efficiently **at *ca*. 600 °C**

25% 50% 75% 10 000 h



Metal supported PCC architecture



Processing < 1000 °C in air

- 1 μm-thick gas-tight electrolyte of BZCY721;
- Porous NiO-BZCY cathode.

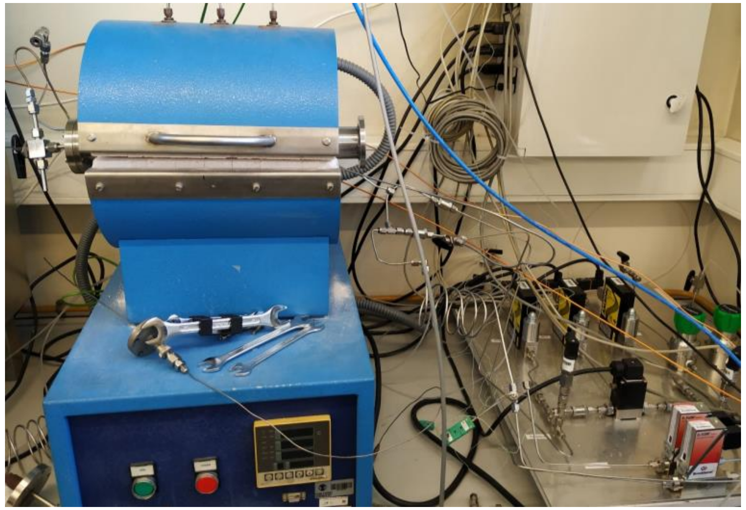
Project Progress/Actions - Aspects

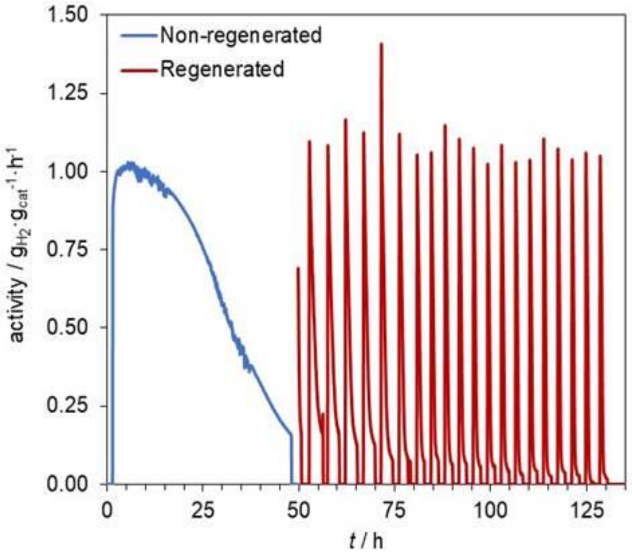
Reactor (3) — WP4

Reactor running the MD reaction for H_2 production ($> 0.45\ g_{H2}\cdot g_{Cat}^{-1}\cdot h^{-1}$)

25% 50% 75%

≤ 5 % activity loss after 10 000 h

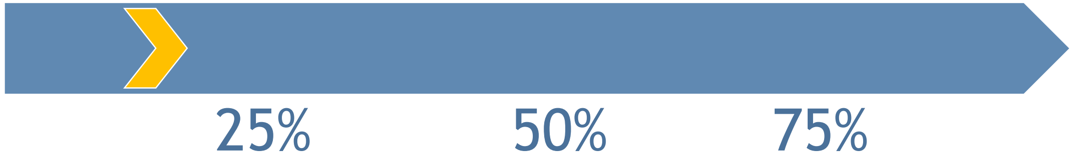




Project Progress/Actions - Aspects

WP5 — **Demonstrative prototype**, integrating the MD catalyst and PCC cell, displaying a loss of performance < 5 %

WP6 — Validate the technology potential on payback energy, levelized cost of energy, **life cycle and environmental assessment and social impact**



WP7 — **Building-up of an interdisciplinary community** and creation of an innovation ecosystem

Exploitation Plan

1 Catalyst

tuning metal-support interaction,
size-controlled synthesis

2 Proton conducting ceramics (PCC)

cost-competitive system for H_2 electrochemical pumping

3 Reactor

new, extremely compact and stable reactor for conducting the MD reaction with catalytic regeneration

4 Prototype/ Pilot Station

System integration and demonstration

- Generation of know-how and intellectual property;
- Licensing;
- New applications/projects benefiting from these developments

- Increase TRL;
- Patenting;
- Test in other locations/applications;
- New applications/projects benefiting from this know-how;
- Generation of intellectual property.

Exploitation Plan

5 Environmental and economic sustainability

6 Social assessment
for assisting in communicating the project to the various stakeholders

7 Training in emerging topics
open Days (open labs) for students and early-stage researchers; final symposium/workshop

8 Build-up of interdisciplinary community and creation of an innovative ecosystem

- Generation of know-how;
- Advertise the cost-efficient and eco-friendly characteristics of the solution;
- Recommendations for new applications/projects;
- Social inquiries;
- New services offered.

- Promotion of process;
- Intensification of PhD;
- Grants for scholarships.

- Budget to third-parties: 206 k€
- 2 monetary prices for potential end-users;
- 3 grants: donation to NGOs; scholarships; helping in the technology scale-up;

Expected Impacts

- **Methane Decomposition:**

Hydrogen
- Dispatchable hydrogen to match with renewable energy production;
- Low cost;

CO_2
- Negative CO_2 emissions – when using biomethane;
- No CO_2 emissions – when using NG;

Carbon
- Use for the construction industry;
- Coating roads (when slightly hydrogenated);
- Electrodes for sodium batteries.

CO_2 sequestration
- Biomethane Decomposition, transforms atmospheric CO_2 into solid carbon, mimicking Nature, @competitive costs.

Expected Impacts

- **112CO2:**

Characteristics of the 112CO2 methane decomposition reactor:

- High density energy reactor - > 10 kW/L;
- Low temperature operation, between 500 °C / 550 °C;
- No byproducts other than Carbon (100 % selective);
- Compatible with mobility applications;
- Low cost reactor and process.

Catalyst:

- Engineered catalyst, catalyst support and reactor;
- Stable operation;

Spin-off effects:

- Address systems with coke deposition – *e.g.* reforming-SOFC, catalysts.

112CO2

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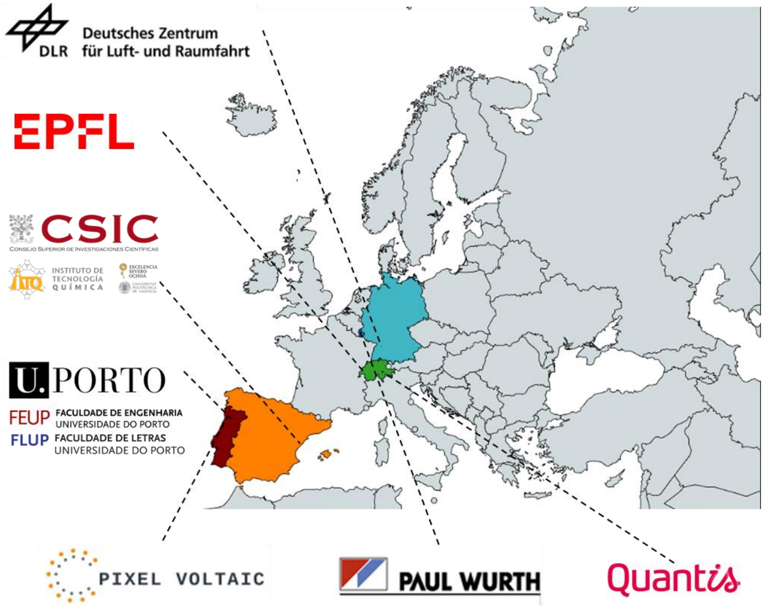

Thank you for your attention!

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Back-up Slides

Assumptions:

CCS cost – 4.4 €/kmol (100 €/ton);

CO_2 – 60 €/ton;

Natural gas produces 9 kg of CO_2 per kg of H_2;

Natural gas cost – 10.9 €/kmol, 627 €/ton (45 €/MWh) – Sept/2021;

BioMethane cost – 7.81 €/kmol, 488 €/ton (35 €/MWh) – Sept/2020;

Based just on the costs of the thermodynamic energy:

Hydrogen from Methane Decomposition (**NatG**) – **2.84 €/kg** H_2; 56.7 €/MWh (0.851 mol of CH_4 per H_2)

Hydrogen from Methane Decomposition (**BioG**) – **2.21 €/kg** H_2; 66.3 €/MWh (0.567 mol of CH_4 per H_2);