Hydrogen Storage via Liquid Organic Hydrogen Carrier (LOHC)

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Structure of the HI ERN as part of the Forschungszentrum Jülich



Forschungszentrum Jülich (FZJ)

- National research institution for interdisciplinary research in the fields of energy, information and bioeconomy
- Part of the Helmholtz Gemeinschaft Deutscher Forschungszentren
- Located at Jülich in North Rhine-Westphalia with several field offices

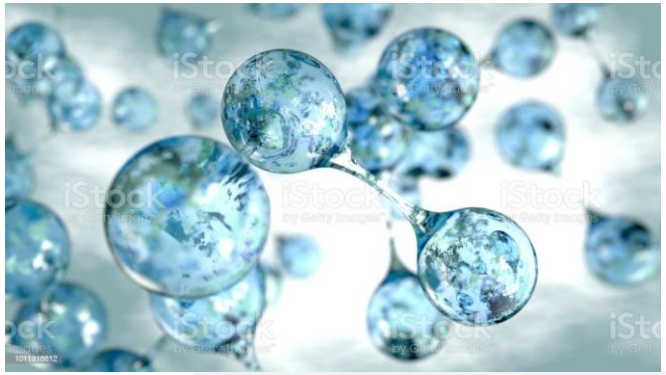




Goals and research focus of HI ERN

Research for a climate-neutral, sustainable and cost-effective energy supply of the future

- Development of material- and process-based solutions for climate-neutral energy generation at acceptable costs for the population
- Combining the excellent research of all partners involved (FZJ, FAU, HZB) in the fields of materials, energy and process research
- Structural and functional characterisation, modelling, production and use of innovative materials for the fields of photovoltaics and hydrogen technologies



Hydrogen as energy vector



Printable Photovoltaics

Why is there a need for chemical hydrogen storage?

- **Climate change is a global challenge**
  → energy transition technologies must function worldwide
- **Climate change is an urgent problem**
  → infrastructure-compatible technologies are required
- **Renewable electricity production is fluctuating**
  → storage technologies required
- **Electricity from renewables is cheap at suitable locations**
  → global trading of renewable energy is expected

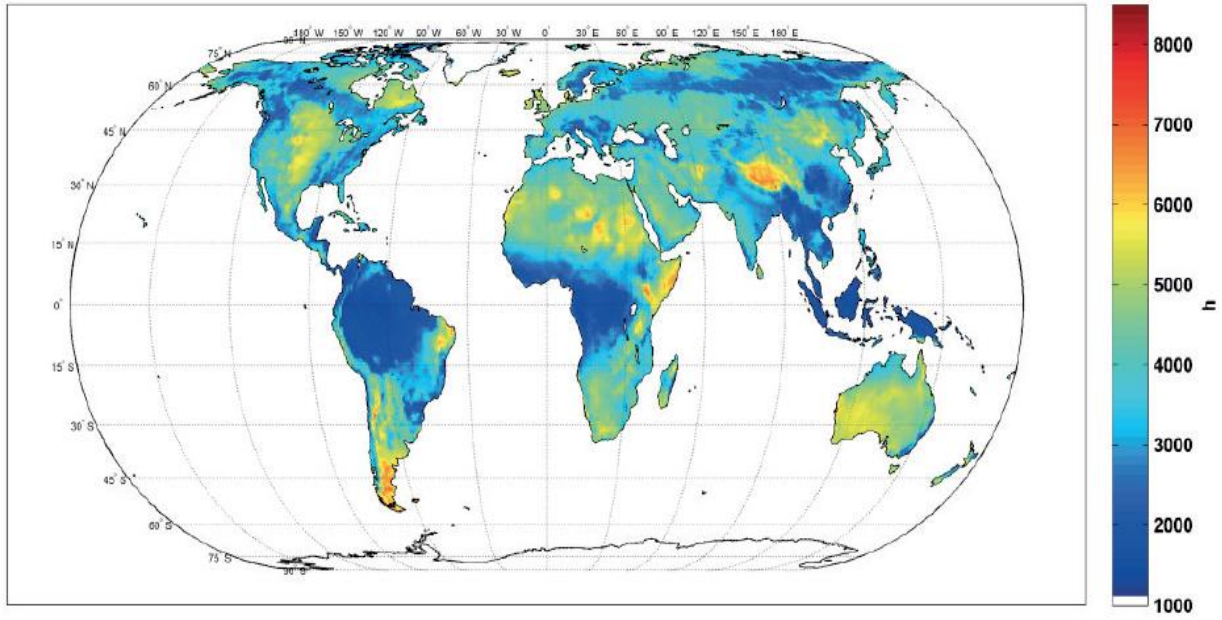




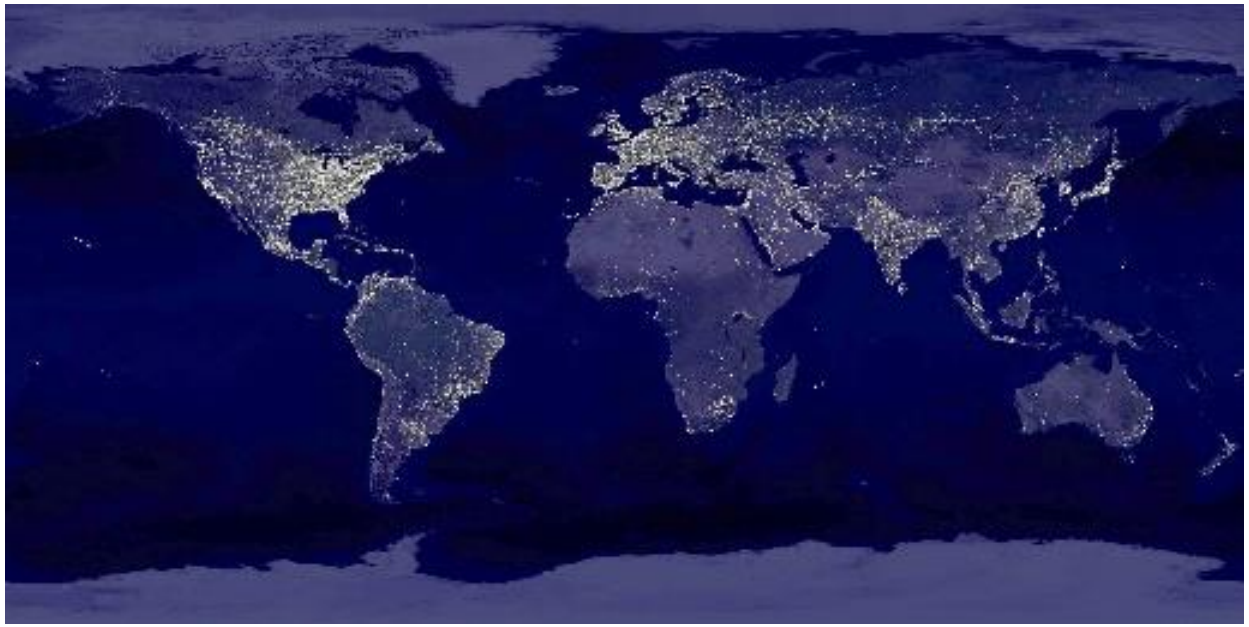




Renewable energy potentials and energy needs are in mismatch



IEA (2017) Renewables



https://earthobservatory.nasa.gov

The defossilized energy system of the future





Electricity from wind, sun and hydropower

Battery electric storage systems

Water electrolysis

Re-electrification using fuel cells

Turbine

Heat pump, electric heating

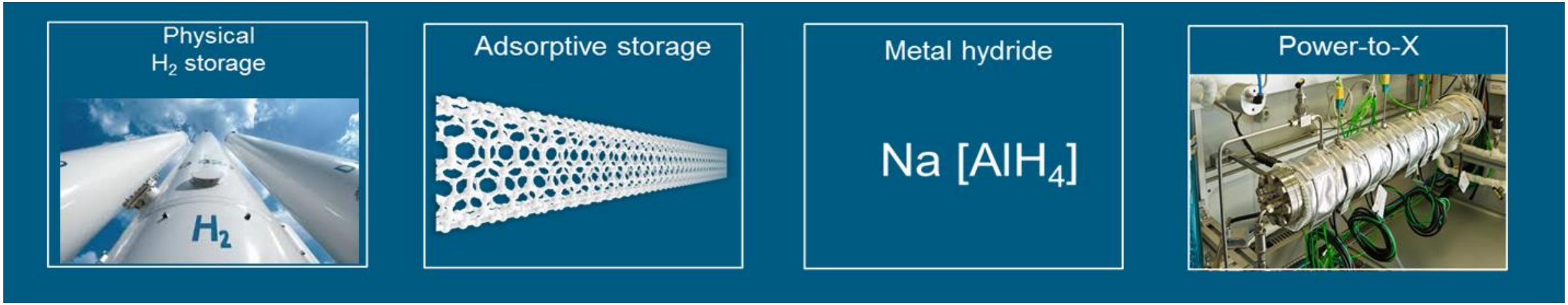
H_2 and H_2 derivatives:
Hydrogen transport and storage; utilization in the industry and mobility sectors

Heat

Combustion, combined heat and power generation

Hydrogen Storage Technologies

- **Hydrogen with excellent gravimetric storage density (33,3 kWh / kg)**
- **Volumetric storage density of hydrogen very low (3 Wh / L @ 1 bar, 20 °C)**



- **Liquid H_2 @ -253 °C**
- **Compressed H_2 @ 300 – 700 bar**

Adsorption on

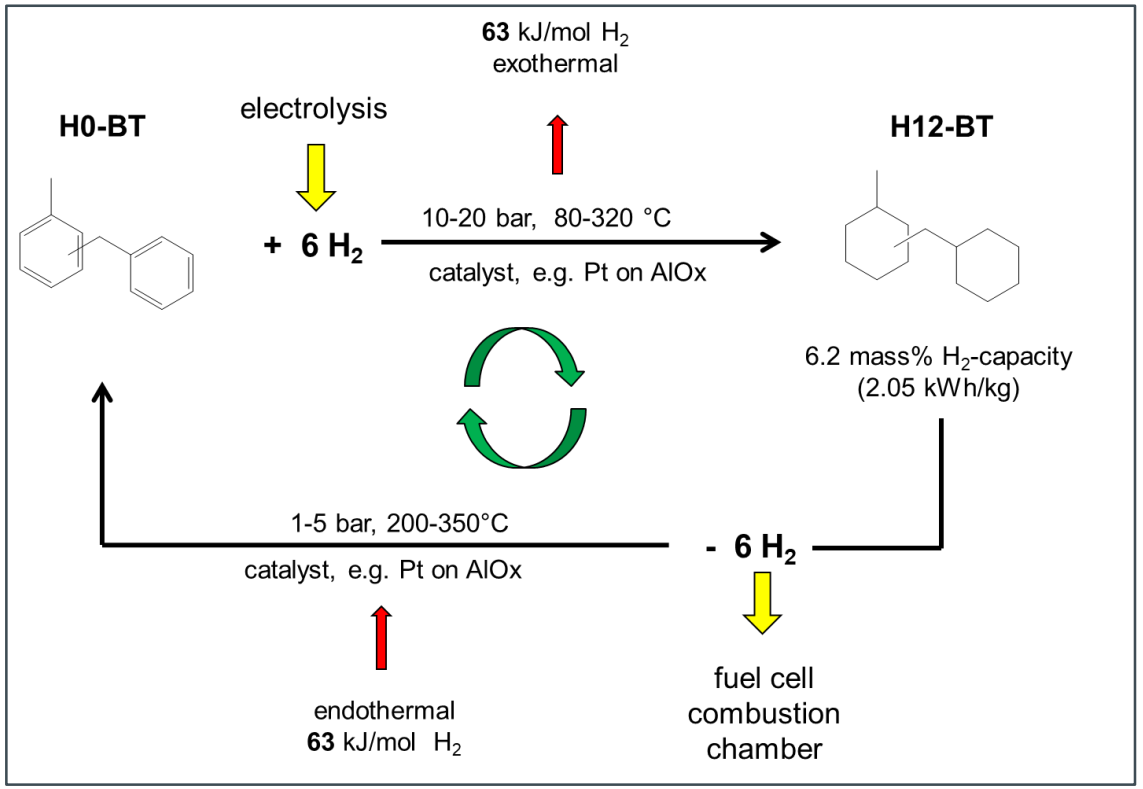
- Fullerenes
- Nanotubes
- Zeolithe
- MOFs

- **Reaction of H_2 with metals**

- **Hydrogenation of CO_2 or N_2**
- **LOHC**

Hydrogen storage via LOHC

- LOHC is not consumed in storage cycle
- Heat release in hydrogenation; heat demand in dehydrogenation
- Storage and transportation of LOHC fluids at ambient conditions possible
- Established heat transfer fluids since 1960s

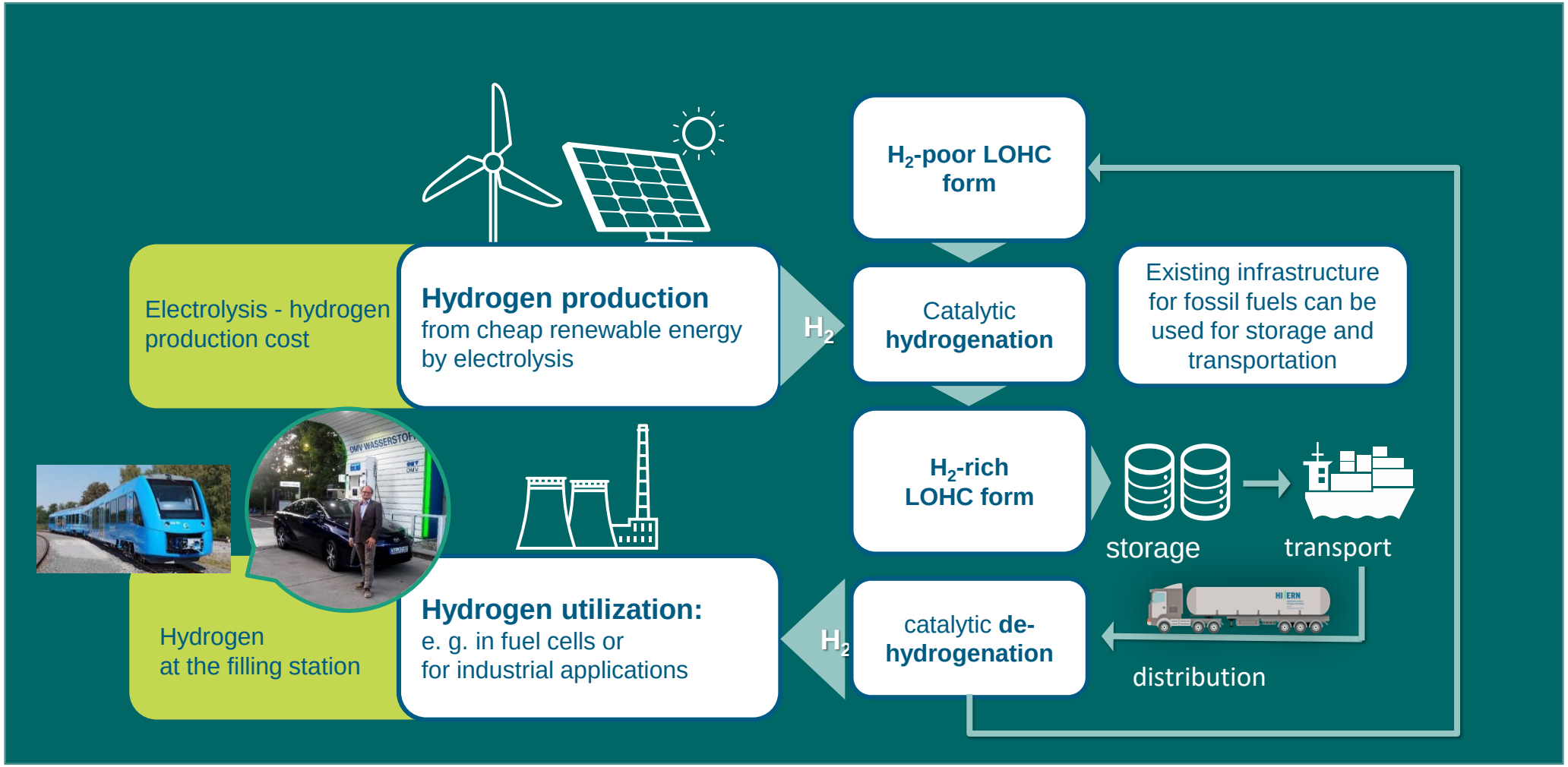




57 kg



LOHC as H_2 transport vector



Relevance of the LOHC-Technology

- **LOHC officially highlighted in the current draft of the revised German national hydrogen strategy:**

“As part of the IPCEI Hydrogen, we intend to fund several projects to research LOHC storage and transport technology from 2023. With this promising future technology, it should be possible in particular to carry out longer ship transports economically and safely, as will be necessary for imports outside the EU and with EU neighboring countries.”

- **LOHC officially highlighted in the European hydrogen strategy:**

“Transport can happen as pure gaseous or liquid hydrogen, or bound in bigger molecules that are easier to transport (e.g. ammonia or liquid organic hydrogen carriers). Hydrogen can also provide cyclical or seasonal storage, e.g.in salt caverns, to produce electricity to cover peak demand, secure hydrogen supply, and allow electrolysers to operate flexibly.”

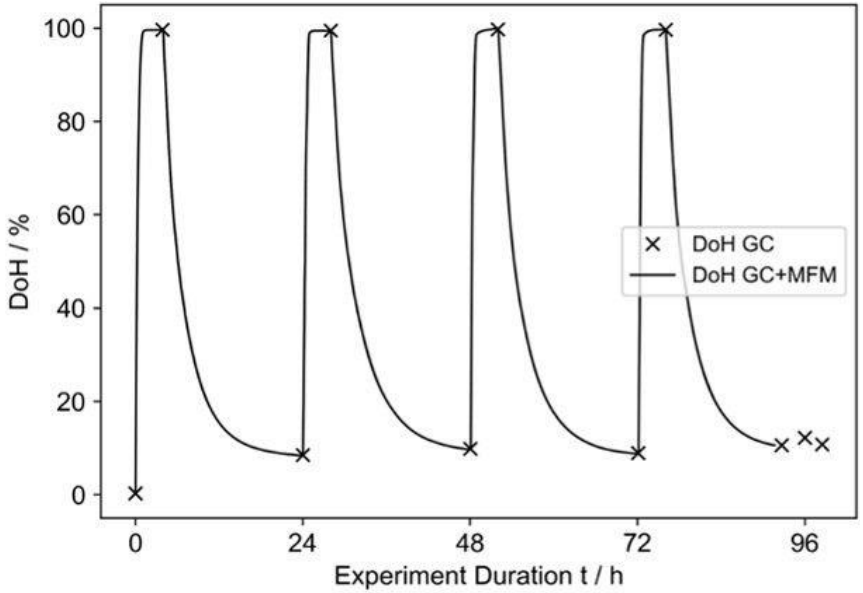
H0-BT / H12-BT our LOHC-system of choice

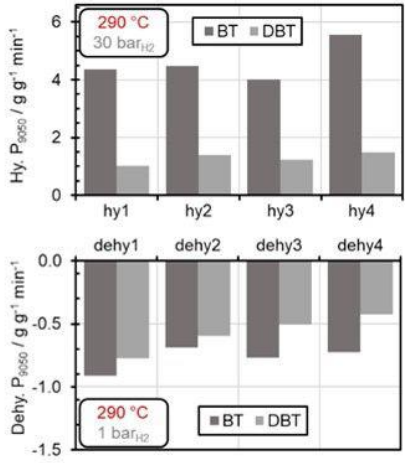
- **Higher boiling point than toluene / methyl cyclohexane**
  → easier separation of LOHC and hydrogen

- **Higher density than toluene / methyl cyclohexane**
  → higher volumetric storage capacity

- **Lower viscosity than dibenzyltoluene / perhydro dibenzyltoluene**
  → easier handling

- **Better hydrogenation and dehydrogenation performance than dibenzyltoluene / perhydro dibenzyltoluene**





(1) Rüde, T., Dürr, S., Preuster, P., Wolf, M., & Wasserscheid, P. (2022). Benzyltoluene/perhydro benzyltoluene–pushing the performance limits of pure hydrocarbon liquid organic hydrogen carrier (LOHC) systems. *Sustainable Energy & Fuels*, *6*(6), 1541-1553.

Safety of LOHC-Technology

Video

LOHC-Dehydrogenation

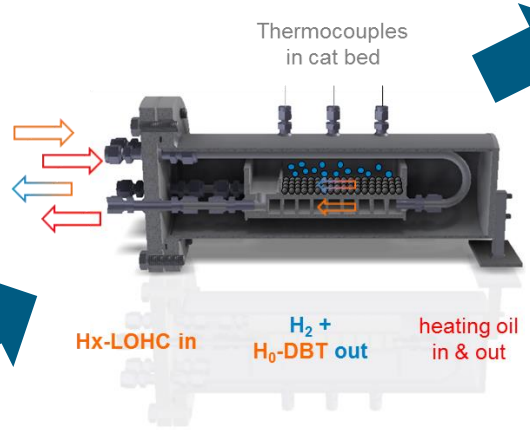
Video

LOHC dehydrogenation: Multiscale aspects in the technology development

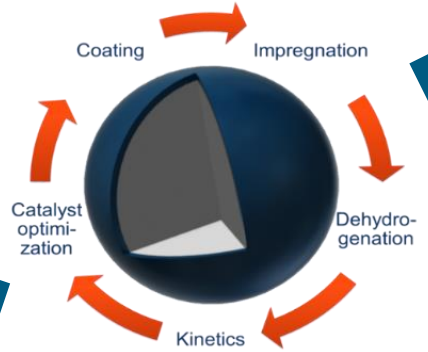
Storage unit scale:
Optimizing heat integration aspects



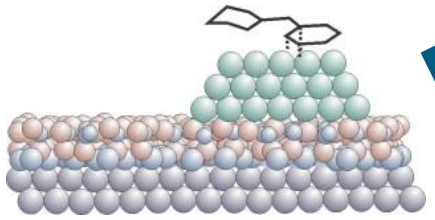
Reactor scale:
Optimizing mass and heat transfer



Mesoscale:
Optimizing mass transfer at the catalyst pellet level

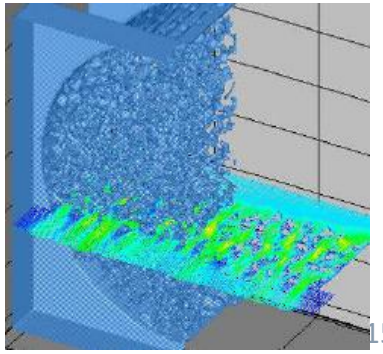


Nanoscale:
Optimizing the active catalytic site



Theory & simulation: DFT, CFD, mass & heat balances

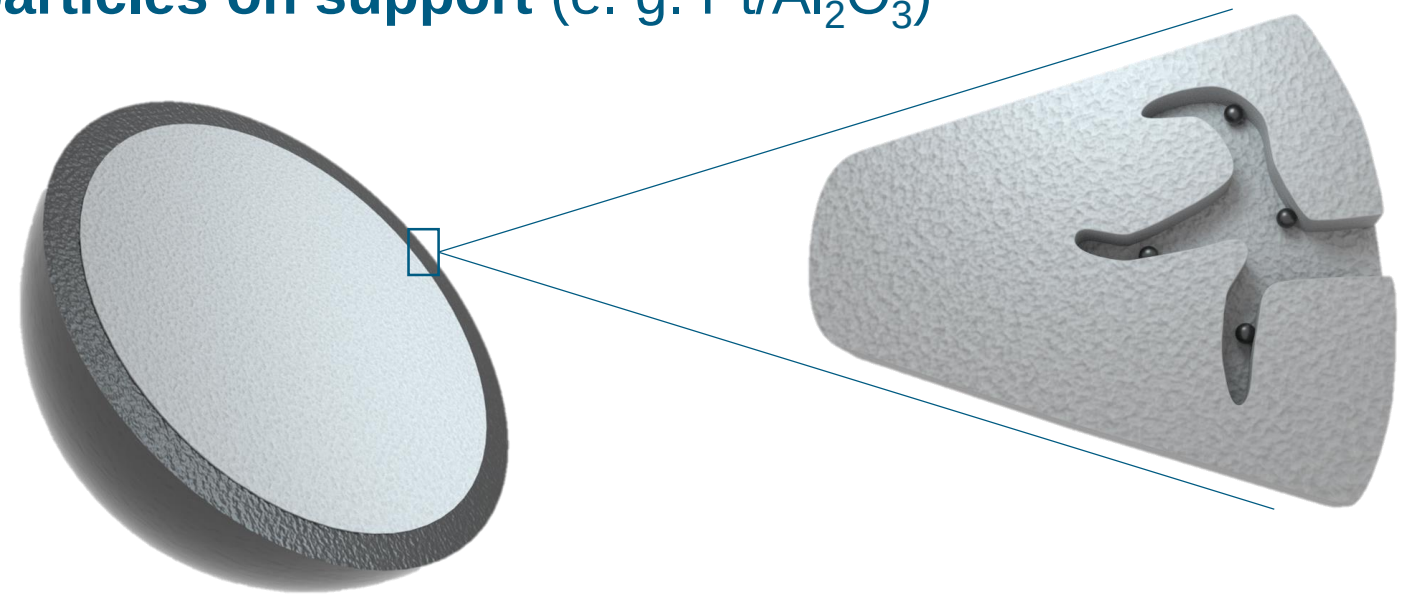




(1) Preuster, P., Papp, C., & Wasserscheid, P. (2017). *Accounts of chemical research*, *50*(1), 74-85.

Catalyst development aspects

Precious metal nanoparticles on support (e. g. Pt/Al_2O_3)



Support (e.g. Al_2O_3)

- Dispersion and stabilisation of nanoparticles
- internal interface, pore size, surface acidity

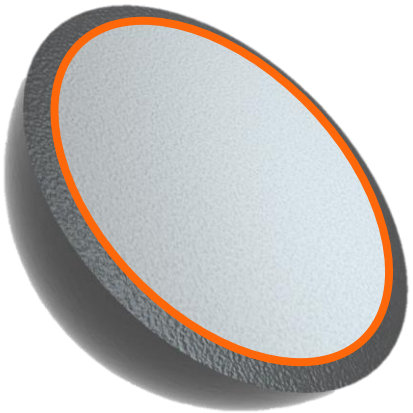
interaction ⟷

Pt nanoparticle

- active sites for dehydrogenation
- Particle size (share of low-coordinated sites) and Pt distribution within the pellet

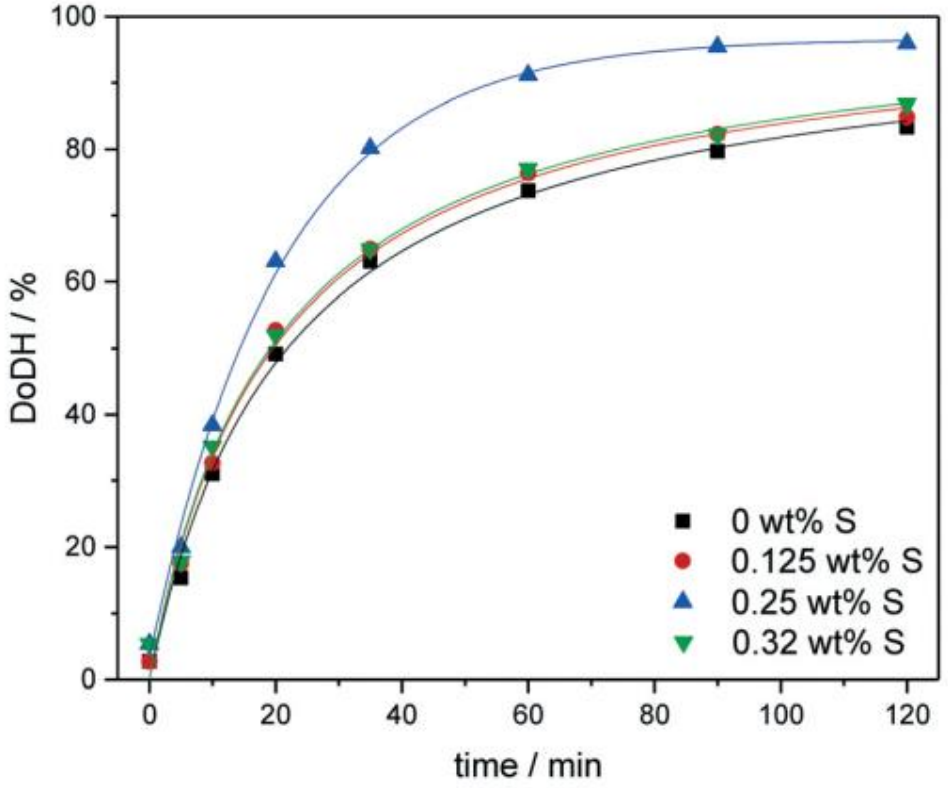
Catalyst development aspects

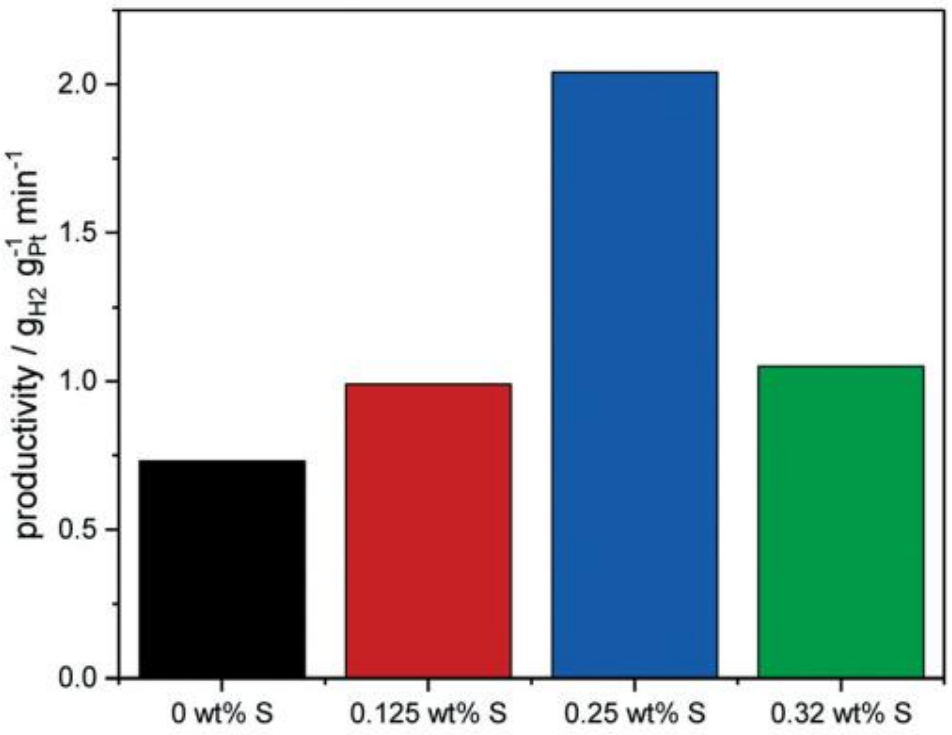
- **Desired properties (from our current knowledge) for LOHC dehydrogenation catalysis:**
- **Low acidity**
- **MgO and TiO_2 are attractive alternatives to standard AlOx supports**
- **Low internal surface (but high enough for good Pt dispersion)**
- **Large pores (> 10 nm) and/or eggshell impregnation and/or thin coatings**
- **Smaller Pt nanoparticles are more active;**
- **Pt particles show a maximum in undesired oxidative cyclization (fluorene formation) at a particle size of 1.5 nm**

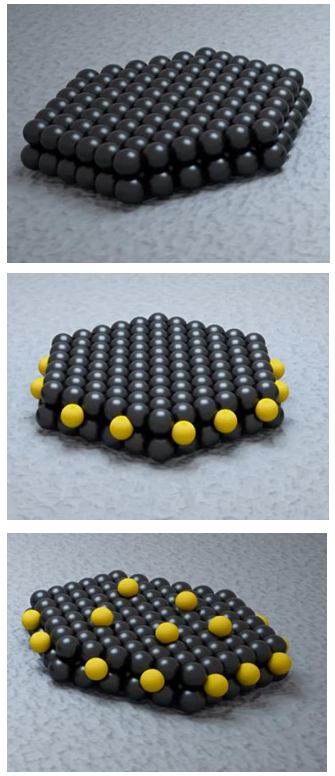


(1) Auer, F., Hupfer, A., Bösmann, A., Szesni, N., & Wasserscheid, P. (2020). Influence of the nanoparticle size on hydrogen release and side product formation in liquid organic hydrogen carrier systems with supported platinum catalysts. *Catalysis Science & Technology*, *10*(19), 6669-6678.

Catalyst development aspects – Partial poisoning with sulfur compounds







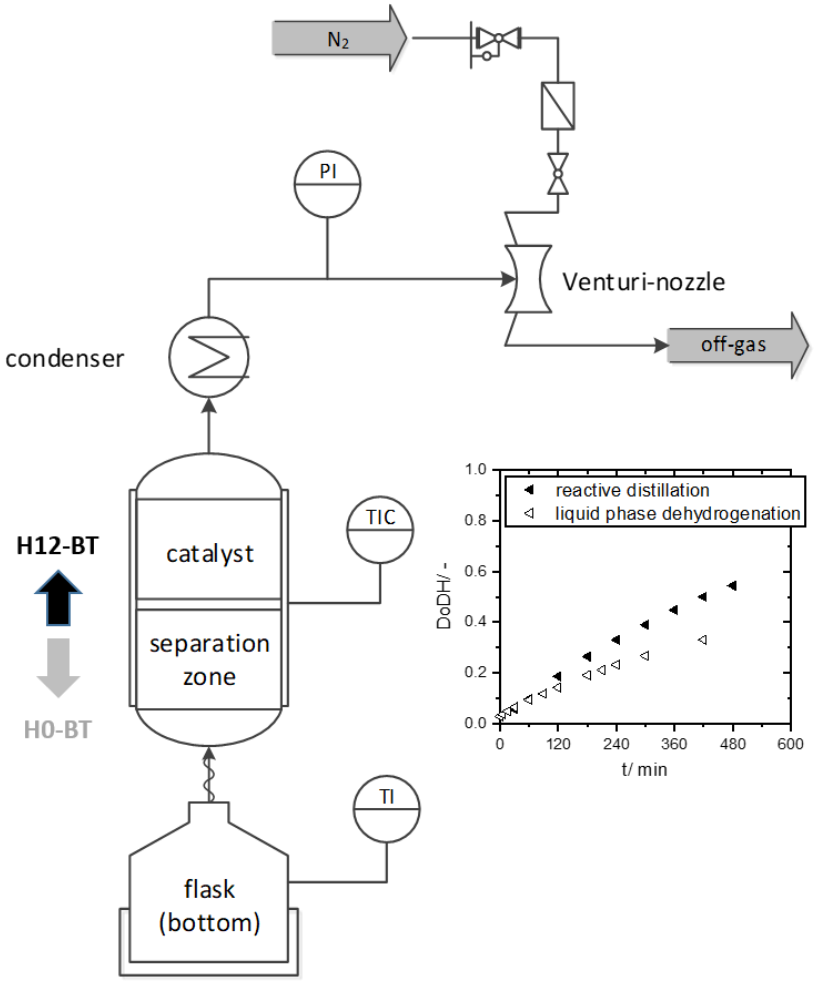
Degree of dehydrogenation (DoDH) over time (left) and productivity of H18-DBT dehydrogenation (middle) with S-modified Pt on alumina catalysts (schematic view, right) - Conditions: 310 °C; 1 bar; LOHC/Pt= 1000.

(1) Auer, F., Blaumeiser, D., Bauer, T., Bösmann, A., Szesni, N., Libuda, J., & Wasserscheid, P. (2019). Boosting the activity of hydrogen release from liquid organic hydrogen carrier systems by sulfur-additives to Pt on alumina catalysts. *Catalysis science & technology*, *9*(13), 3537-3547.

Development of innovative reactor concepts

Reactor scale(1)

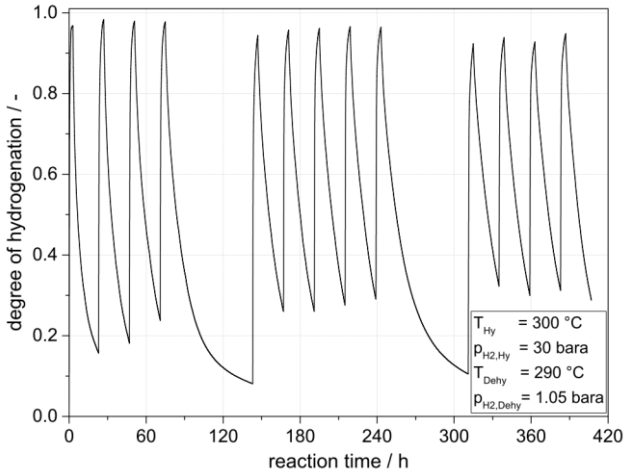
- Dehydrogenation of H12-BT by reactive distillation
- Decrease of reaction temperature down to 200 °C by vacuum operation possible
- Increase of activity and selectivity by integrated product separation
- Increase of efficiency by coupling dehydrogenation with a HT-PEM fuel cell(2,3)



(1) Geißelbrecht, M., Mrusek, S., Müller, K., Preuster, P., Bösmann, A., & Wasserscheid, P. (2020). *Energy & Environmental Science*, *13*(9), 3119-3128.
(2) Lee, K. S., Maurya, S., Kim, Y. S., Kreller, C. R., Wilson, M. S., Larsen, D., ... & Mukundan, R. (2018). *Energy & Environmental Science*, *11*(4), 979-987.
(3) Chaichi, A., Venugopalan, G., Devireddy, R., Arges, C. G., & Gartia, M. R. (2020). *ACS Applied Energy Materials*.
(4) Rüde, T., Lu, Y., Anschütz, L., Blasius, M., Wolf, M., Preuster, P., ... & Geißelbrecht, M. *Energy Technology*.

Stationary hydrogen storage by the *OneReactor* concept

- **Conducting hydrogenation and dehydrogenation in one reactor, with the same catalyst**
- **Change between reactions by pressure adjustment**
- **Reduction of investment and operating cost**
- **Successful demonstration since 2017**
- **Upscaling of the reactor in commissioning**





(1) Jorschick, H., Preuster, P., Dürr, S., Seidel, A., Müller, K., Bösmann, A., & Wasserscheid, P. (2017). *Energy & Environmental Science*, *10*(7), 1652-1659.
(2) Jorschick, H., Dürr, S., Preuster, P., Bösmann, A., & Wasserscheid, P. (2019). *Energy Technology*, *7*(1), 146-152.
(3) Geiling, J., Steinberger, M., Ortner, F., Seyfried, R., Nuss, A., Uhrig, F., ... & Preuster, P. (2021). Combined dynamic operation of PEM fuel cell and continuous dehydrogenation of perhydro-dibenzyltoluene. International Journal of Hydrogen Energy, 46(72), 35662-35677.

The Project Living Lab Energy Campus



Photovoltaic
(1.5 MW)



2 Batteries
(2 MW / 2 MWh)



Electrolyser
(400 kW)



Fuel Cell
(100 kW)



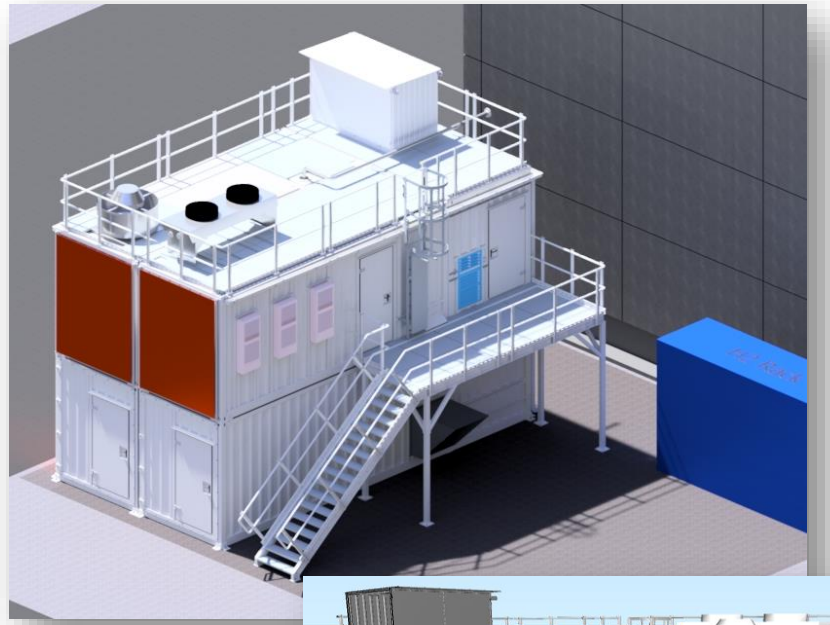
Waste heat grid
(1.2 MW)



LOHC-System
(300 kW / 150 MWh)

OneReactor-concept in the LLEC project

- **Heat release and demand time-shifted**
- **CHP-unit heat controlled**
  - Heat generation by increasing the power of the gas engines
  - Reduction of the power of the gas engines possible, when heat is transferred from the OneReactor to the heat grid
- **Increasing the efficiency of LOHC storage cycle by sector coupling**

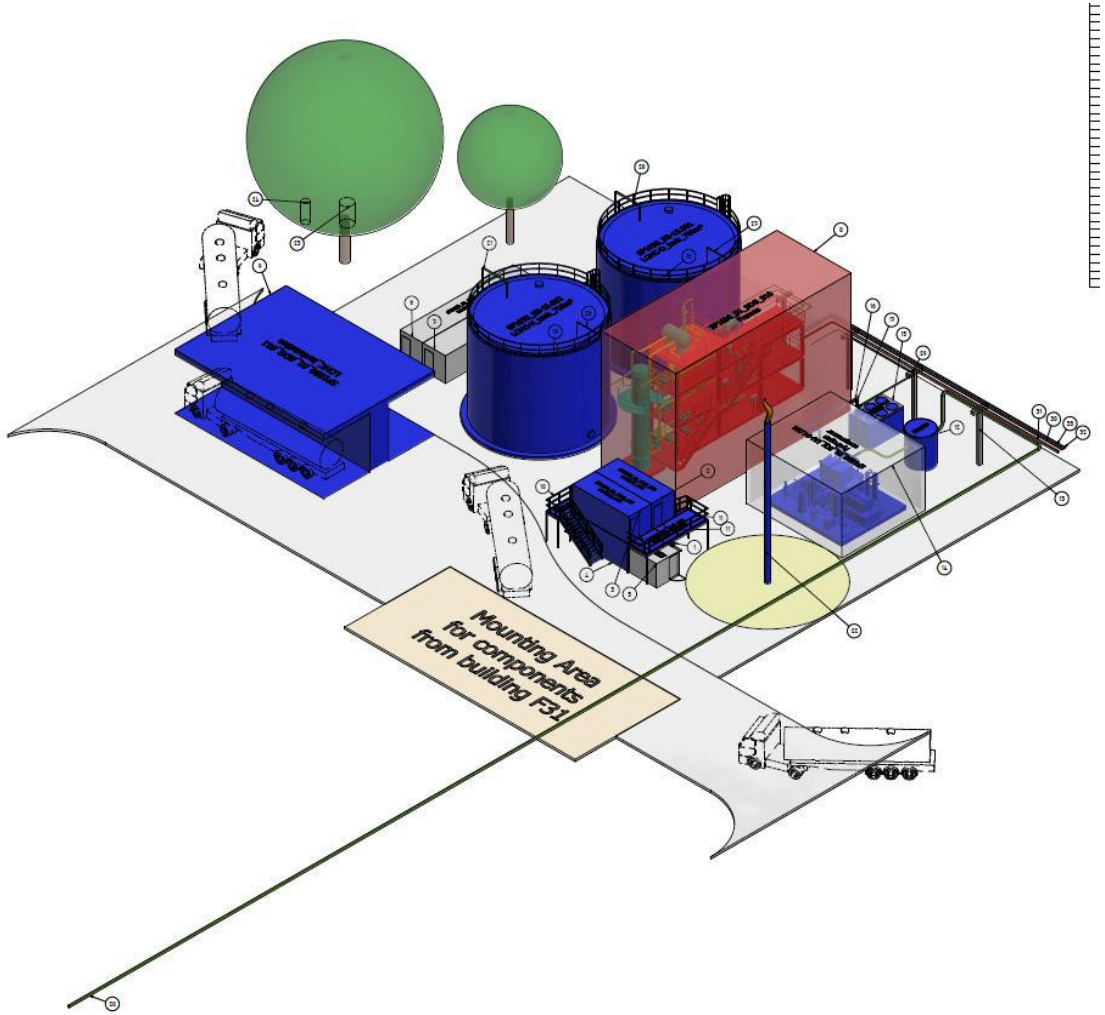




HECTOR Project

System-Scale

- **Construction of a hydrogenation plant in industrial scale by the industrial partner LOHC Industrial Solutions NRW GmbH**
- **Location: Chempark Dormagen**
- **Accompanying research by HI ERN**
  - Detection and quantification of impurities
  - Development of purification strategies
  - Identification of the influence of impurities on the LOHC process

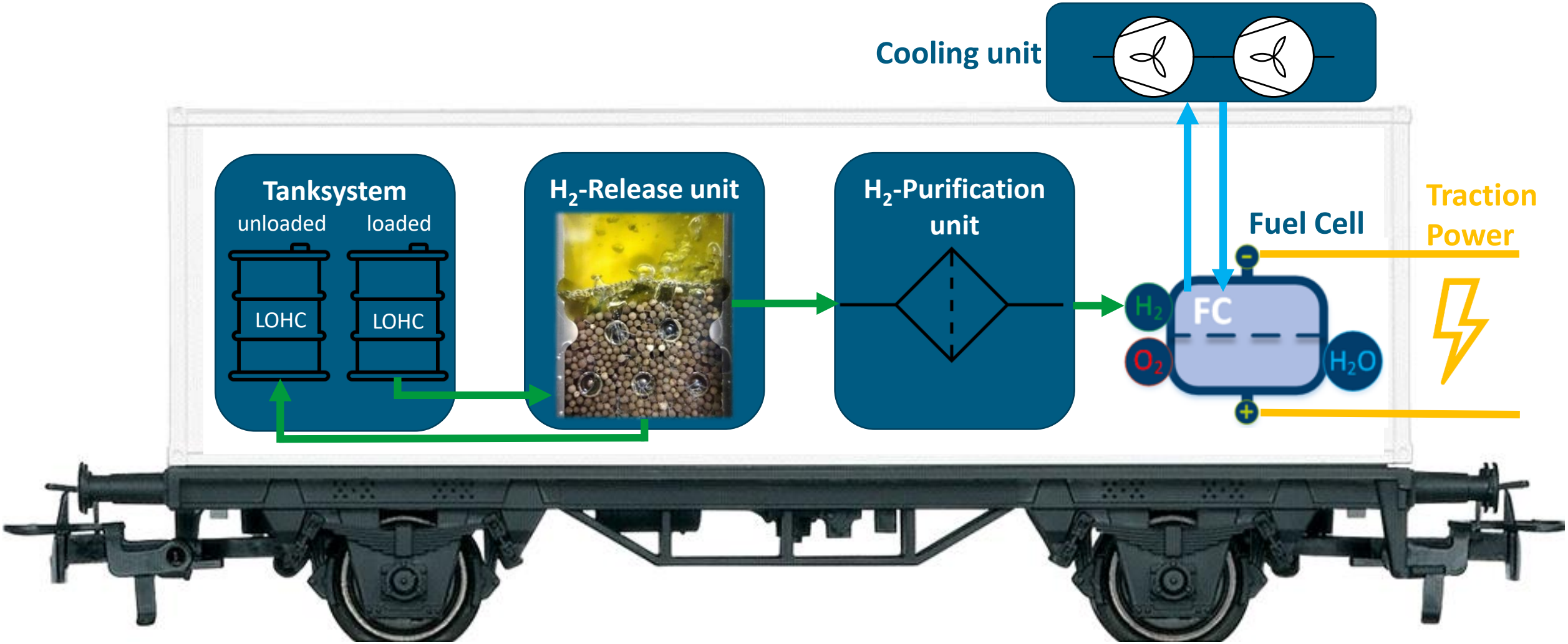


(1) https://hydrogenious.net/kick-off-for-construction-and-operation-of-the-worlds-largest-plant-for-storing-green-hydrogen-in-liquid-organic-hydrogen-carrier/

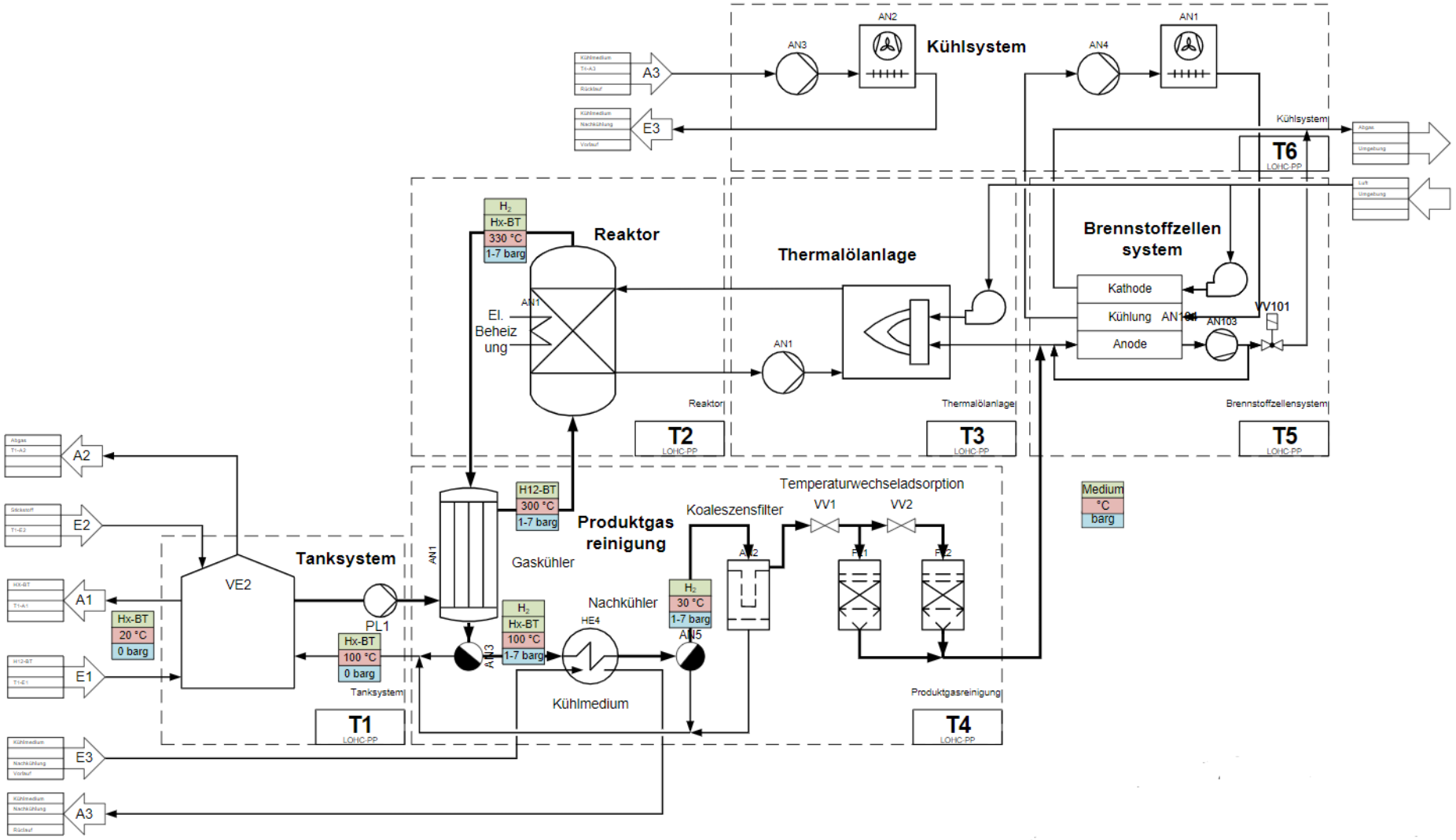
Train Project

- Financed by the Bavarian Ministry of Economic Affairs, Regional Development and Energy
- Research to further develop the LOHC-Technology
- Development of a train supplied by LOHC-bound hydrogen (demonstration unit)
- On board release of the LOHC-bound hydrogen and conversion of hydrogen to electricity by a fuel cell
- First operation of the demonstration unit planned in 2025

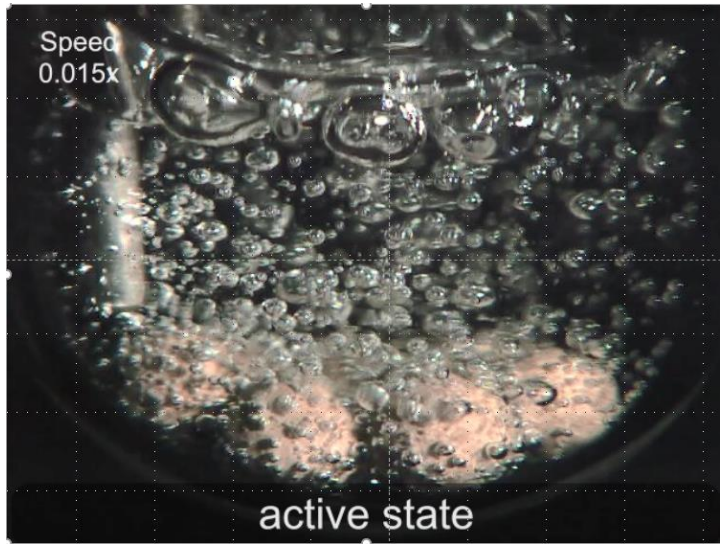
Train project

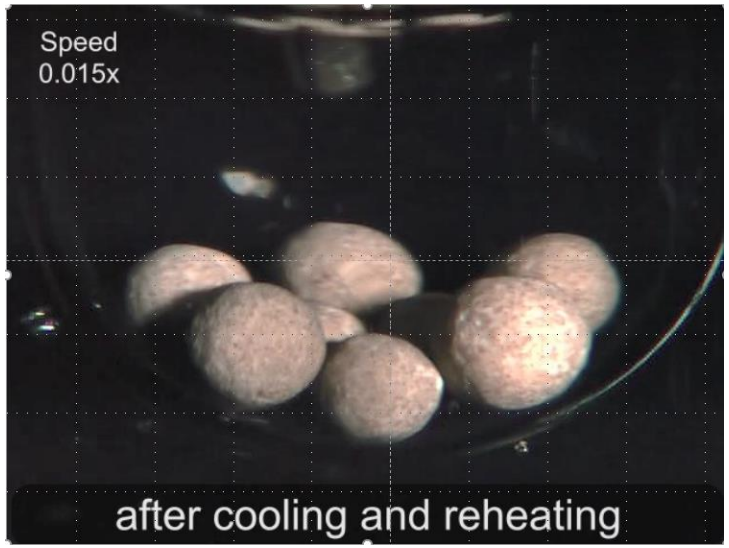


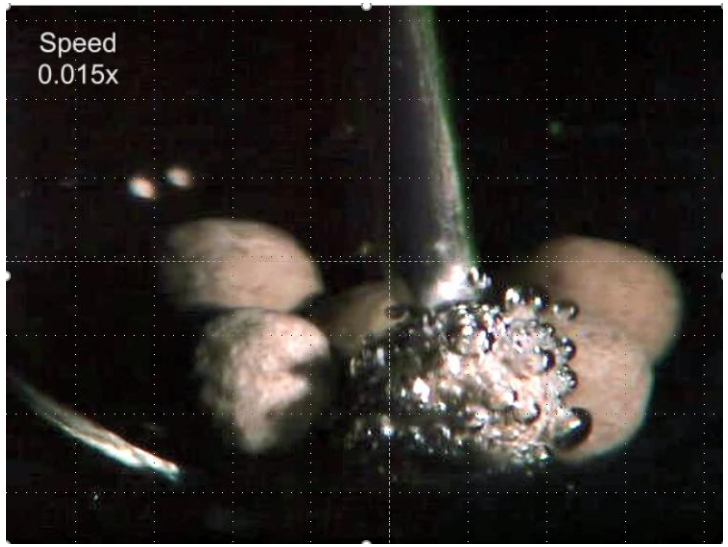
PFD of the hydrogen release unit



Bubble nucleation as rate determining step

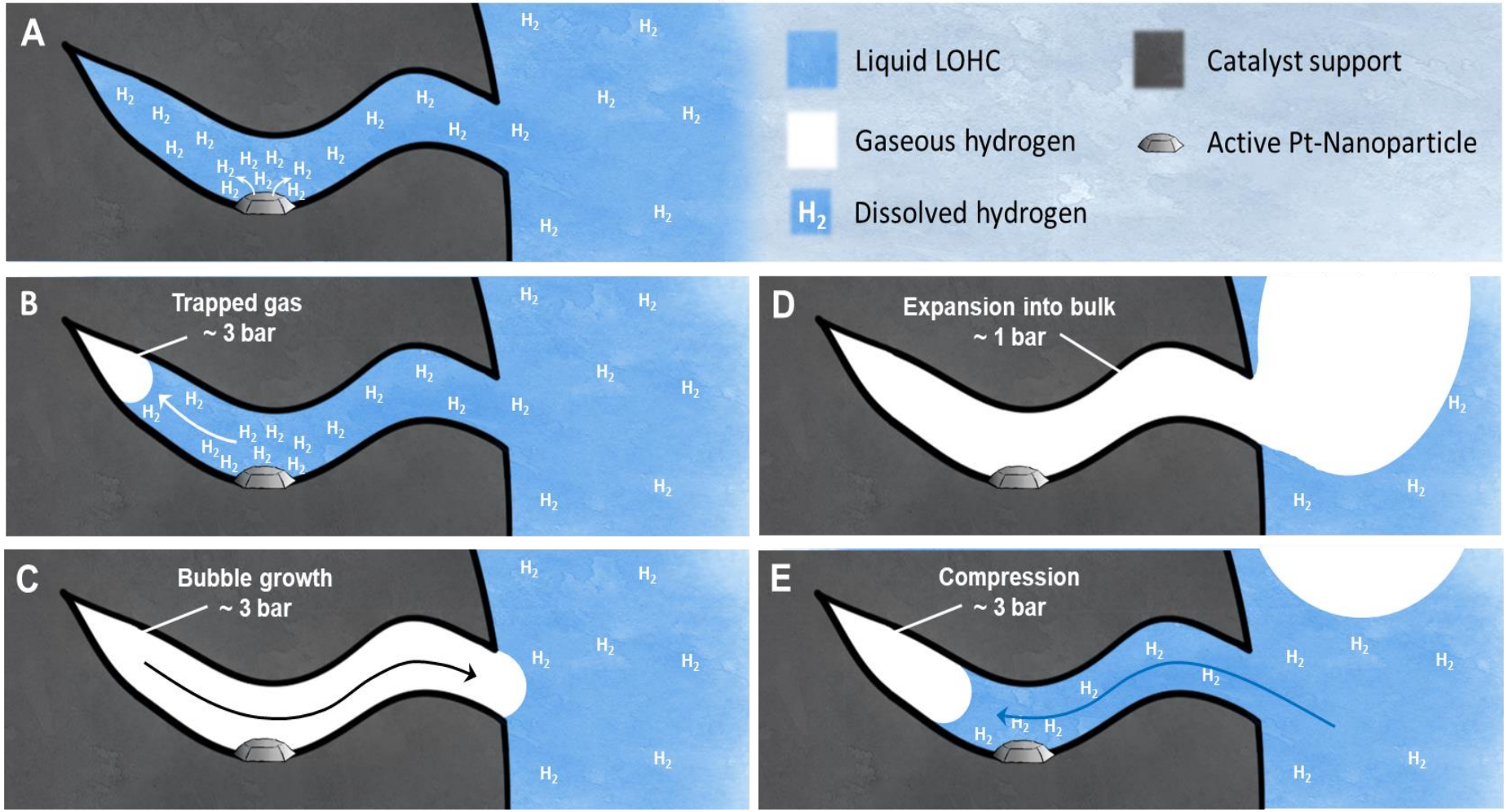






(1) Solymosi, T., Geißelbrecht, M., Mayer, S., Auer, M., Leicht, P., Terlinden, M., ... & Wasserscheid, P. (2022). Nucleation as a rate-determining step in catalytic gas generation reactions from liquid phase systems. *Science Advances*, *8*(46), eade3262.

Bubble nucleation as rate determining step



A: diffusive mass transport of dissolved hydrogen in the ‘inhibited pellet’

B-E: time frames of oscillating convective mass transport by bubble growth, expansion and compression of a fresh catalyst in its ‘active’ state of the pellet

Summary

- Hydrogen transport and storage as one key challenge for a future sustainable energy system
- LOHC as save and efficient option to store and distribute hydrogen
- In LOHC-Technology hydrogen is stored by reversible hydrogenation and dehydrogenation of an liquid organic carrier molecule
- Catalysis, reaction system engineering and heat management as key challenges to refine LOHC-Technology

Thank you for your attention!