Hydrogen storage and distribution via liquid organic carriers

Dr. Martin Johannes Schneider
Hydrogenious Technologies
Germany

Bridging Renewable Electricity with Transportation Fuels Workshop
August 27-28, 2015
BROWN PALACE HOTEL, Denver, CO

HYDROGENIOUS TECHNOLOGIES GmbH
Weidenweg 13
91058 Erlangen

hydrogenious TECHNOLOGIES

Hydrogenious Technologies

LOHC Technology

Applications

Products and Projects

Hydrogenious Technologies GmbH – a pioneer in chemical hydrogen storage

- Founded in 2013
- Shareholders:
  - Dr.-Ing. Daniel Teichmann
  - Prof. Wasserscheid, Prof. Arlt, Prof. Schlücker
  - FAU Erlangen
  - Anglo American Platinum
- Headquarters: Erlangen, Germany
- Winner of several start-up competitions
  - German Accelerator
  - Bavarian Founders Price
  - Science4Life Venture-Cup
  - Hochschulgründerpreis Nordbayern

Hydrogenious Technologies offers innovative LOHC systems for energy storage and hydrogen distribution

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hydrogenious DISTRIBUTION

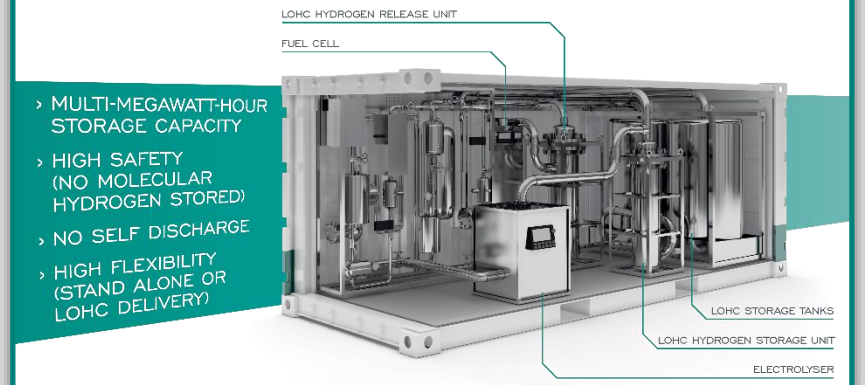
Innovative hydrogen logistics with:

- Industrial hydrogenation units up to 1.500 Nm^3/h H_2
- Easy transport by truck, train or ship – up to 1.800 kg H_2/ 40t-truck
- Safe supply of hydrogen filling stations
- Utilization of existing infrastructure

hydrogenious SYSTEMS

LOHC – Energy storage systems:

- Turnkey plug & play systems and tailored solutions
- 30 – 1000 kW input power
- Storage capacity of 10 – 1000 MWh
- Optimized for local energy storage



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Applications

Products and Projects

Important physical and chemical properties of LOHCs

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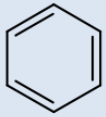
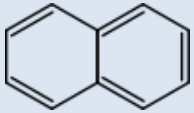
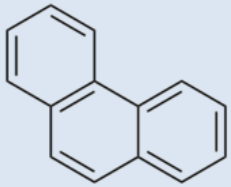
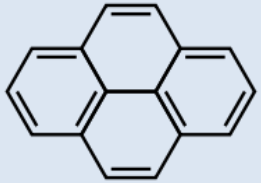
Property	Comment	Applications		
		Mobility	Stationary Storage	Energy Transport
Storage Capacity	max. 7.2 wt.-% for aromatic systems	!!	!	!
Handling	Melting point, boiling point, viscosity	!	o	!!
Thermodyn. Equilibrium	Hydrogenation and dehydrogenation at moderate conditions	!	!	!
Stability	Thermal and chemical	o	!!	!
Toxicity	Transport restrictions	!!	!	!!
Availability	Price, abundance	o	!!	!!

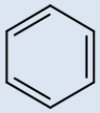
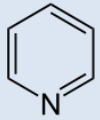
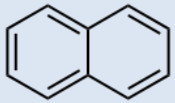
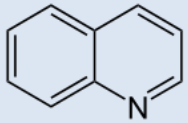
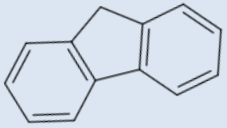
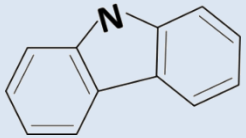
!! Very important ! Important o Neutral

Thermodynamics of LOHCs - Influence of the number of rings on the reaction enthalpy

	Structure	Enthalpy difference
Benzene		$\lvert\Delta^R h\rvert$ = 68,6 kJ/mol
Naphthaline		$\lvert\Delta^R h\rvert$ = 65,3 kJ/mol
Phenanthrene		$\lvert\Delta^R h\rvert$ = 61,9 kJ/mol
Pyrene		$\lvert\Delta^R h\rvert$ = 61,1 kJ/mol

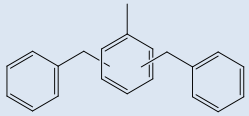
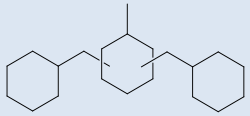
Pez et al., World Pat., WO 2005/000457A2, 2005.

Thermodynamics of LOHCs – Influence of heteroatoms on enthalpy of reaction

	Structure	Enthalpy difference	$\Delta \lvert\Delta H\rvert$
Benzene		$\lvert\Delta^R h\rvert$ = 68,6 kJ/mol	- 3 kJ/mol
Pyridine		$\lvert\Delta^R h\rvert$ = 65,6 kJ/mol	
Naphthaline		$\lvert\Delta^R h\rvert$ = 65,3 kJ/mol	- 3,4 kJ/mol
Chinoline		$\lvert\Delta^R h\rvert$ = 61,9 kJ/mol	
Fluorene		$\lvert\Delta^R h\rvert$ = 60,3 kJ/mol	- 9,3 kJ/mol
Carbazole		$\lvert\Delta^R h\rvert$ = 51,0 kJ/mol	

Pez et al., World Pat., WO 2005/000457A2, 2005.

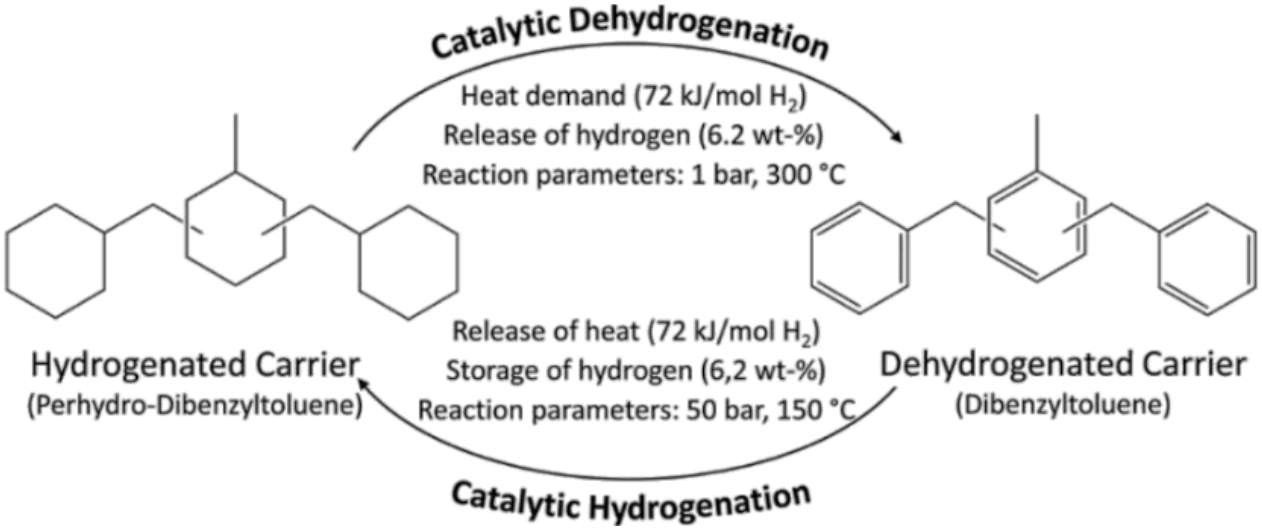
Choice of Liquid Carrier Material: Dibenzyltoluene

Properties		Dibenzyltoluene
Unloaded species		
Loaded species		
Storage density		6,2 wt.-% 1,9 kWh/kg
Handling	Melting point	-34 °C
(loaded)	Boiling point	390 °C
Thermodyn. Equilibrium	Reaction enthalpy	~62 kJ/mol
Toxicity (loaded)		-
Availability	Current price	ca. 4-5 $/kg

Brückner, N.; Obesser, K.; Bösmann, A.; Teichmann, D.; Arlt, W.; Dungs, J.; Wasserscheid, P.: ChemSusChem, 2013.

LOHC enables safe and efficient storage of hydrogen through molecular binding

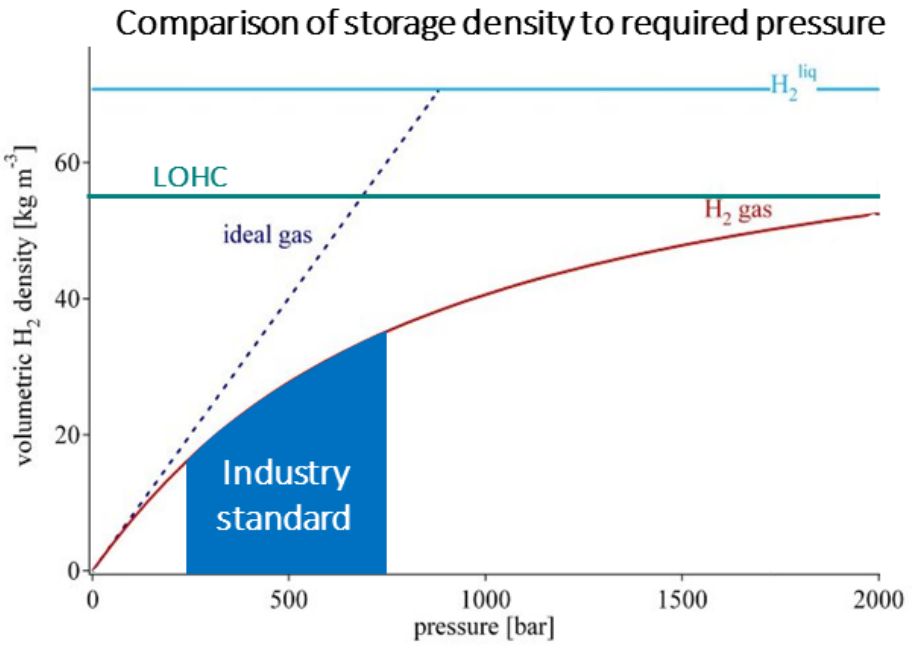
Hydrogen storage is achieved via chemical binding of hydrogen molecules to a liquid organic hydrogen carrier: Dibenzyltoluene



Our LOHC is…

- **Efficient**
  - 624 Nm^3 (57kg) H_2 / m^3 LOHC
  - No self-discharge
- **Safe**
  - No molecular hydrogen – non-explosive
  - LOHC not classified as dangerous good
- **Easy to handle**
  - Handling at ambient conditions
  - Diesel-like liquid – easy transport
- **Low priced**
  - 4-5€/l
  - Industrial heat transfer oil

LOHC technology has the potential to revolutionize hydrogen storage and transport technology



- 3kg of hydrogen @ 300 bar pressure
- Total weight and volume: 242.4kg and >150l

- 3kg of hydrogen in LOHC
- Total weight and volume: 48.15 kg and 52.9 l

Hydrogenious Technologies

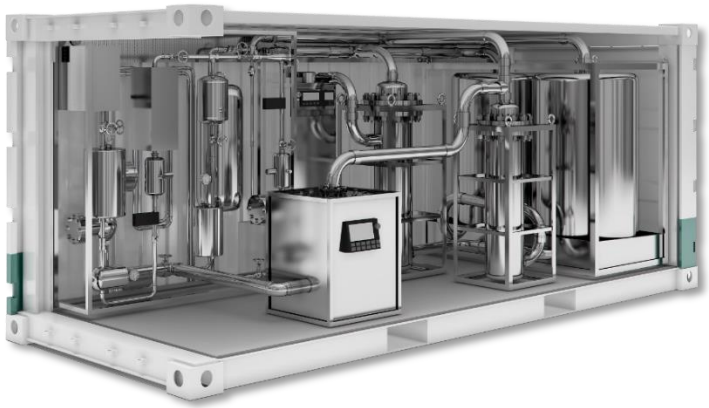
LOHC Technology

Applications

Products and Projects

Hydrogenious Technologies
One technology – two markets

hydrogenious SYSTEMS



Energy Storage

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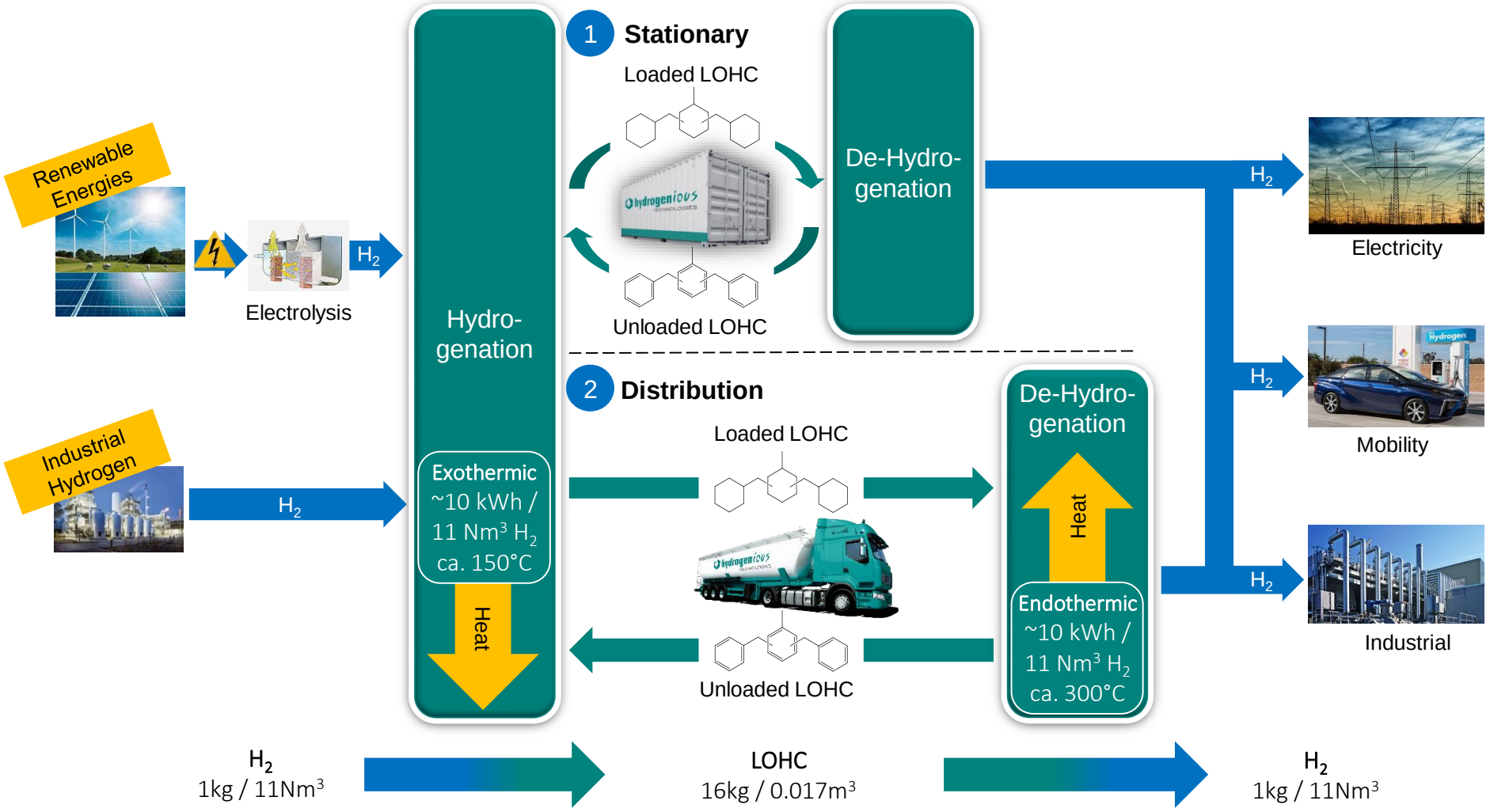
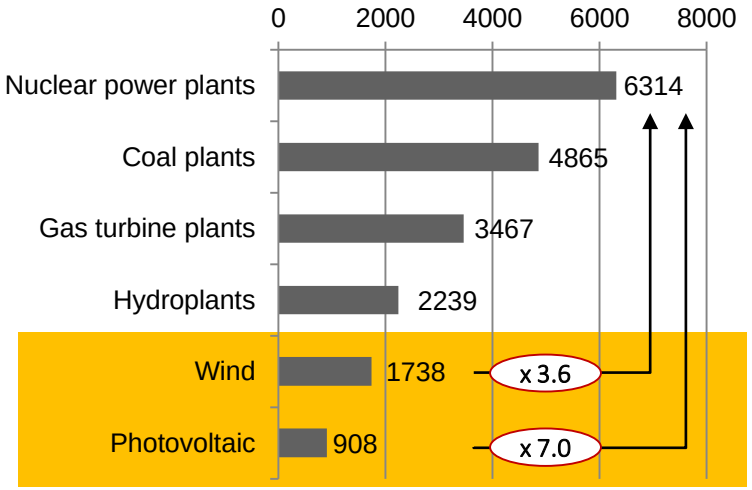
Hydrogen Logistics

Hydrogenious Technologies offers scalable and flexible solutions for storage and utilization of hydrogen



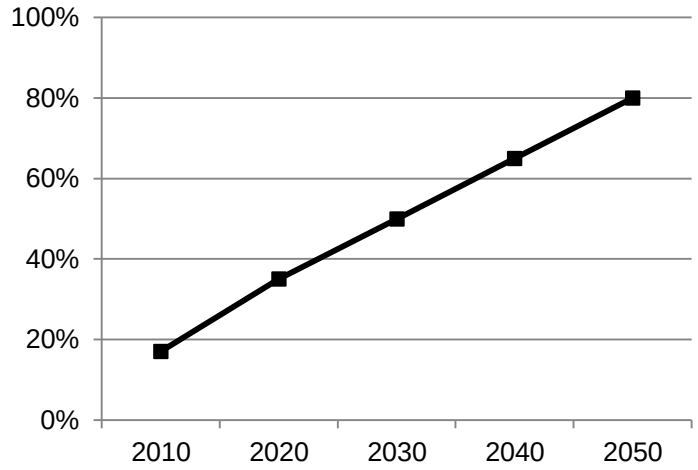
Energy suppliers face significant challenges driven by the expansion of unsteady renewable energies

Number of full load hours of diff. energy producers:



Source: Energy statistics BMWi, 2012

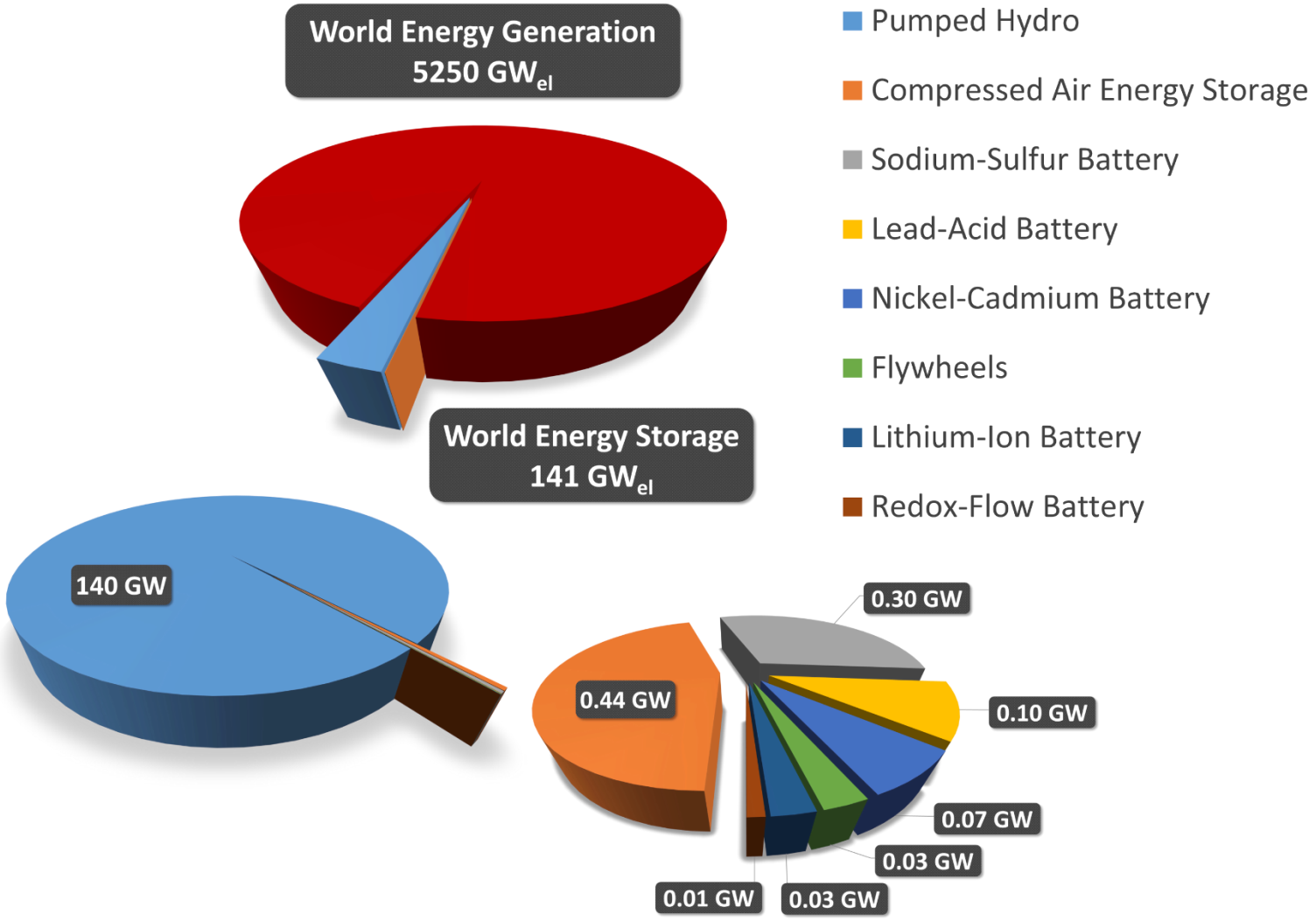
Target share of renewable energies in electricity production in GER:



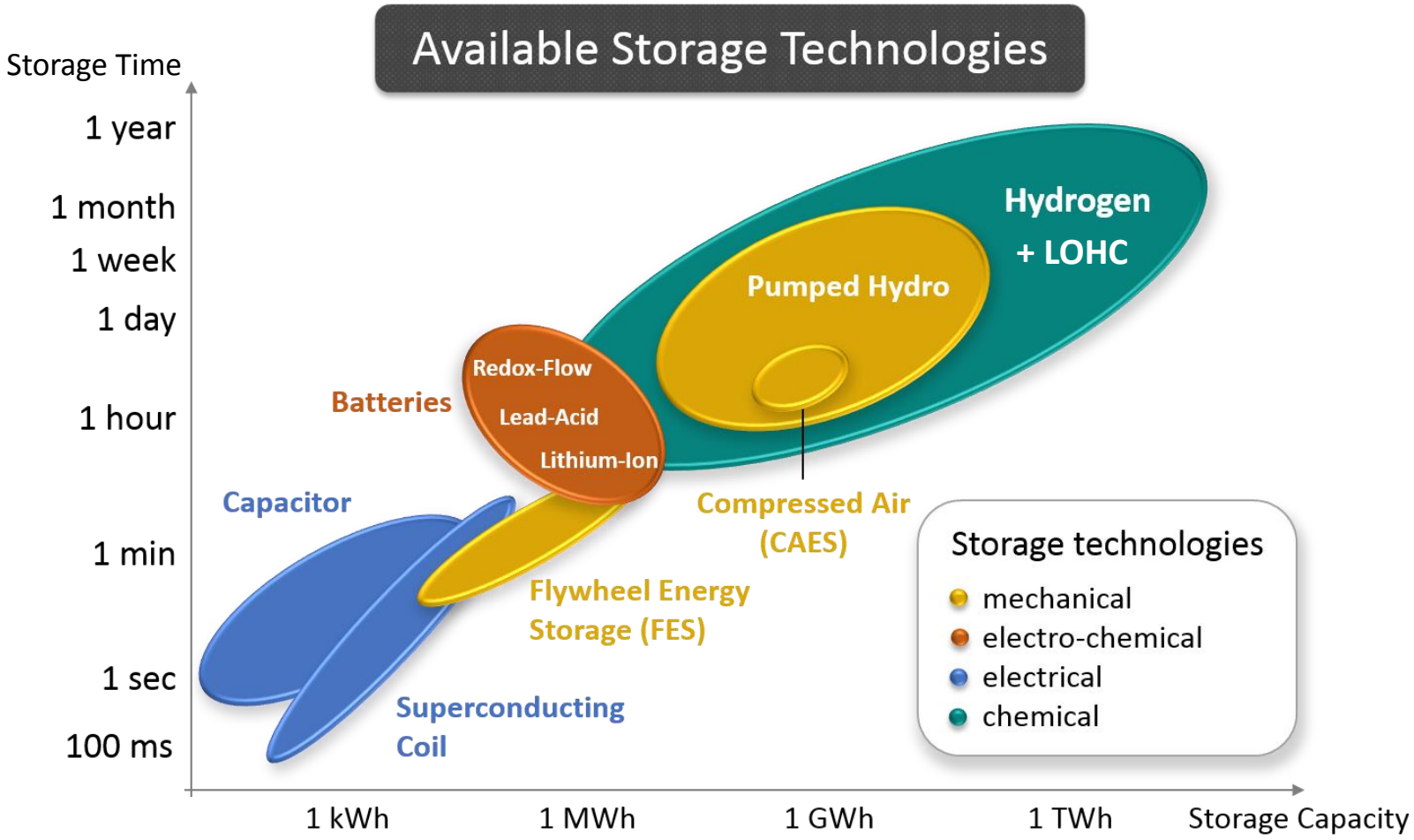
Source: Energy concept of the German government

A safe supply of electricity via renewable energies can only be ensured with significant storage capacities

Grid-scale energy storage solutions are missing to cope with increasing share of fluctuating renewables



Applicability of various storage technologies depends on storage time and capacity



Round-trip electrical efficiency of LOHC storage technology can reach up to 43 %

	PEM o. alkaline electrolysis + PEM-FC	PEM o. alkaline electrolysis + CHP	PEM o. alkaline electrolysis + SOFC	SOEC + SOFC
Elektrolysis	70 %	70 %	70 %	90 %
Hydrogenation	98 %	98 %	98 %	98 %
Dehydrogenation	70 %	98 %	98 %	98 %
Re-electrification	55 %	42 %	50 %	50 %
el. round-trip efficiency	**26 %**	**28 %**	**34 %**	**43 %**
Temperature level of waste heat	up to 150°C	up to 300°C	up to 400°C	up to 400°C

The stationary LOHC energy storage system offers the ideal solution for long-term storage of large amounts of energy

Possible applications

- **Grid support**
  Grid stabilization and balancing of supply / demand peaks
- **Energy production buffering**
  Maximizing usable energy output of wind and PV parks
- **Energy self-supply and autarky**
  Independence from increasing electricity prices
- **Off-Grid and back-up**
  Installation at remote locations and as back-up supply
- **Long term energy storage**
  Seasonal storage of large amounts of energy

Hydrogenious Technologies
One technology – two markets

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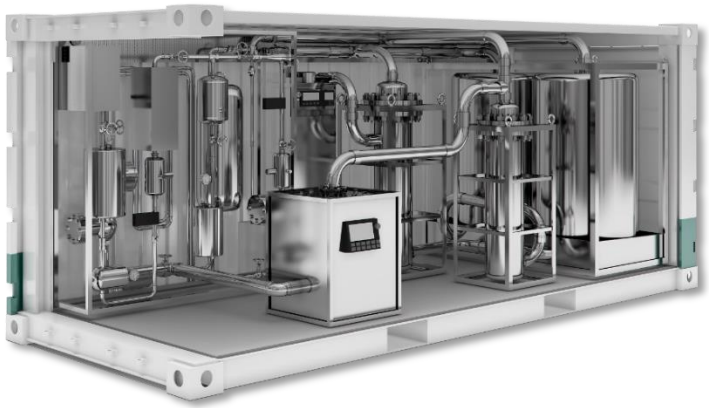

Energy Storage

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Hydrogen Logistics

LOHC-based hydrogen logistics is cheaper, safer and easier than existing CGH2 or LH2 technologies

Industrial H_2 production

H_2 filling stations

Industrial utilization

	H_2 per truck	Capex for trailer	Maintenance intensity	Handling	Hazardous	Net energy required[1] (excl. transport)	Boil-off
LOHC (Perhydro-Dibenzyltoluene)	up to 1.800kg	~50.000€	low	+	no	5-30%[2] (th.)	0%
CGH2 200bar	up to 400kg	>250.000€	very high	-	yes	10-20% (el.) (eq. to 30-60% th.)	0%
LH2 (-253°C)	up to 3.300kg	>500.000€	high	-	yes	30% (el.) (eq. to ~ 90% th.)	1-3% / day

1. In % of lower heating value of stored hydrogen 2. Actual value fully dependent on usage of exothermic heat produced in hydrogenation process

LOHC-based hydrogen logistics have significant advantages in operational handling and costs compared to CGH2

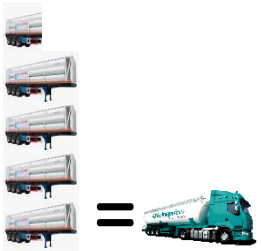
Operational advantages

Handling a liquid at ambient pressure and temperature is **significantly easier** than handling compressed gases or cryogenic liquids

Our LOHC enables a **continuous hydrogenation and dehydrogenation** process, even when exchanging the unloaded vs. loaded LOHC

Dibenzyltoluene (loaded and unloaded with hydrogen) is **non-explosive and less toxic than diesel** – reducing safety and precaution requirements significantly

Opex advantages



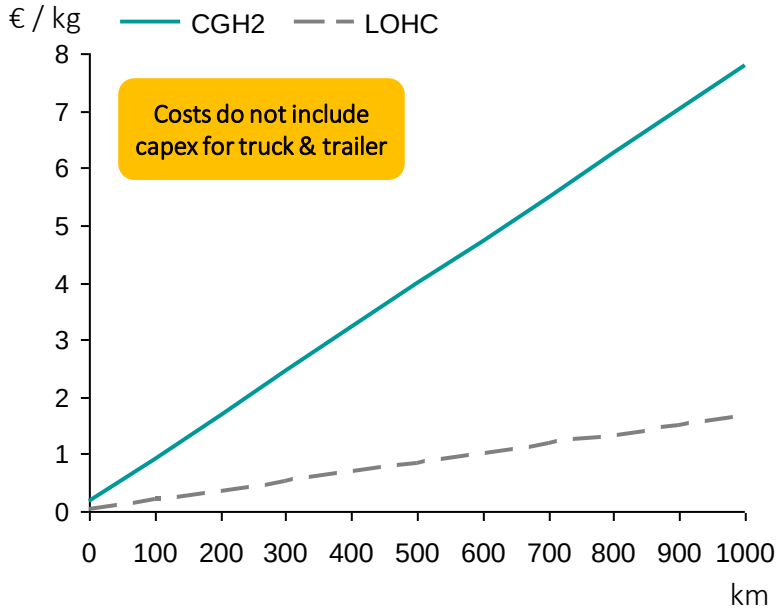
A 40t truck can transport **>4x as much hydrogen** with LOHC compared to 200bar compressed hydrogen tube trailers, **reducing** personnel needs and **transport costs** significantly

Dibenzyltoluene (loaded and unloaded with hydrogen) is **not classified as a dangerous good** – allowing transport through tunnels and cities and therewith **shortening transport routes**

Our LOHC can be **stored and transported in standard diesel tanks**, which only require low maintenance efforts

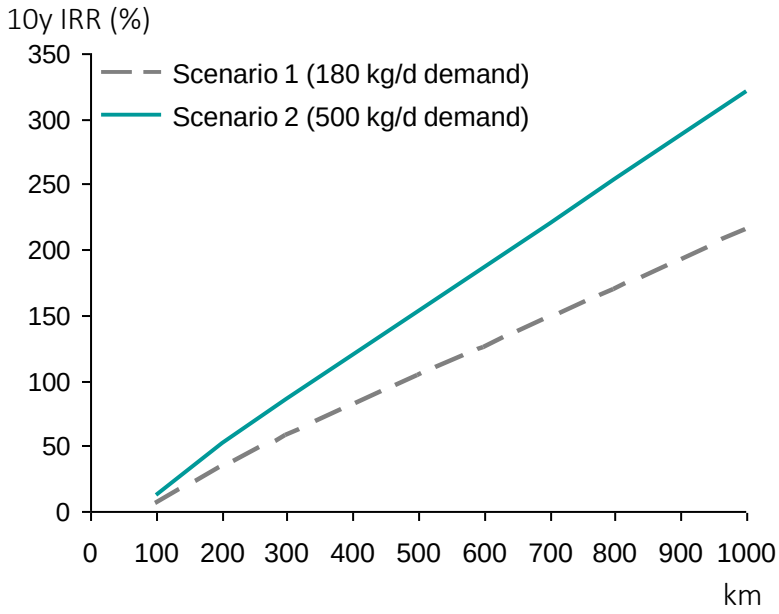
Cost comparison of hydrogen logistics shows clear advantage of LOHC vs. CGH2

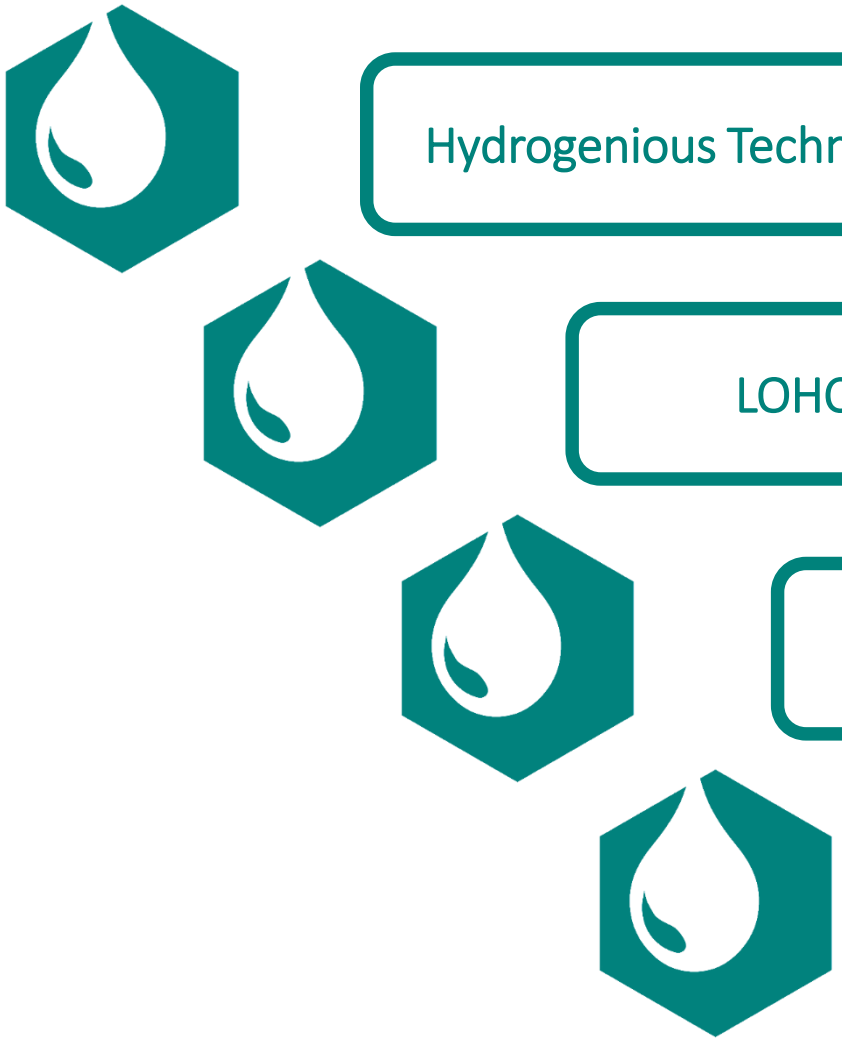
Cash cost of hydrogen transport



	LOHC	CGH2
# of trucks	4.18	18
H_2 per truck	1.722 kg	400 kg

Business case comparison of LOHC vs. CGH2

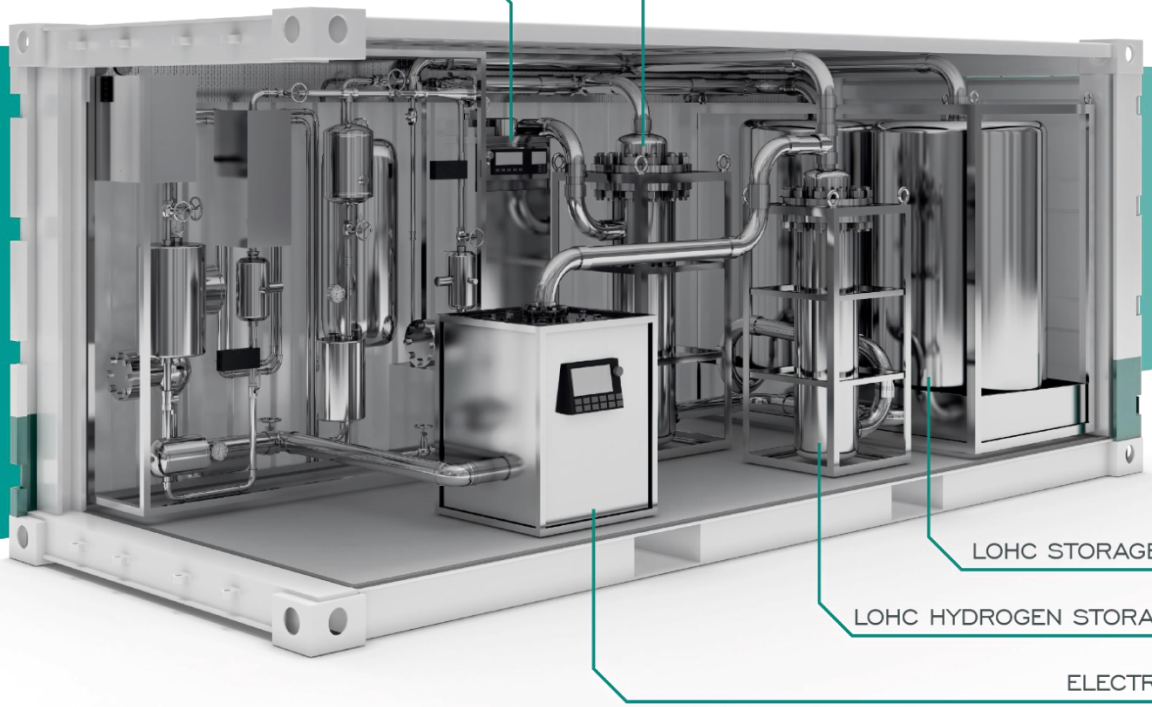



Hydrogenious Technologies
LOHC Technology
Applications
Products and Projects

Hydrogenious Technologies offers an all-in-one solution for efficient hydrogen storage

hydrogenious TECHNOLOGIES

- MULTI-MEGAWATT-HOUR STORAGE CAPACITY
- HIGH SAFETY (NO MOLECULAR HYDROGEN STORED)
- NO SELF DISCHARGE
- HIGH FLEXIBILITY (STAND ALONE OR LOHC DELIVERY)



The road to commercialization

Today | 2017 | 2020+

Hydrogen logistics

Competing Technology:
Compressed gas trucks

Business case (today):

Cost reduction through easy handling and transport

Off-grid energy supply

Competing Technology:
Diesel engines

Business case (2-3 years):

Reduction in costs of operation (no fuel spent, no logistics)

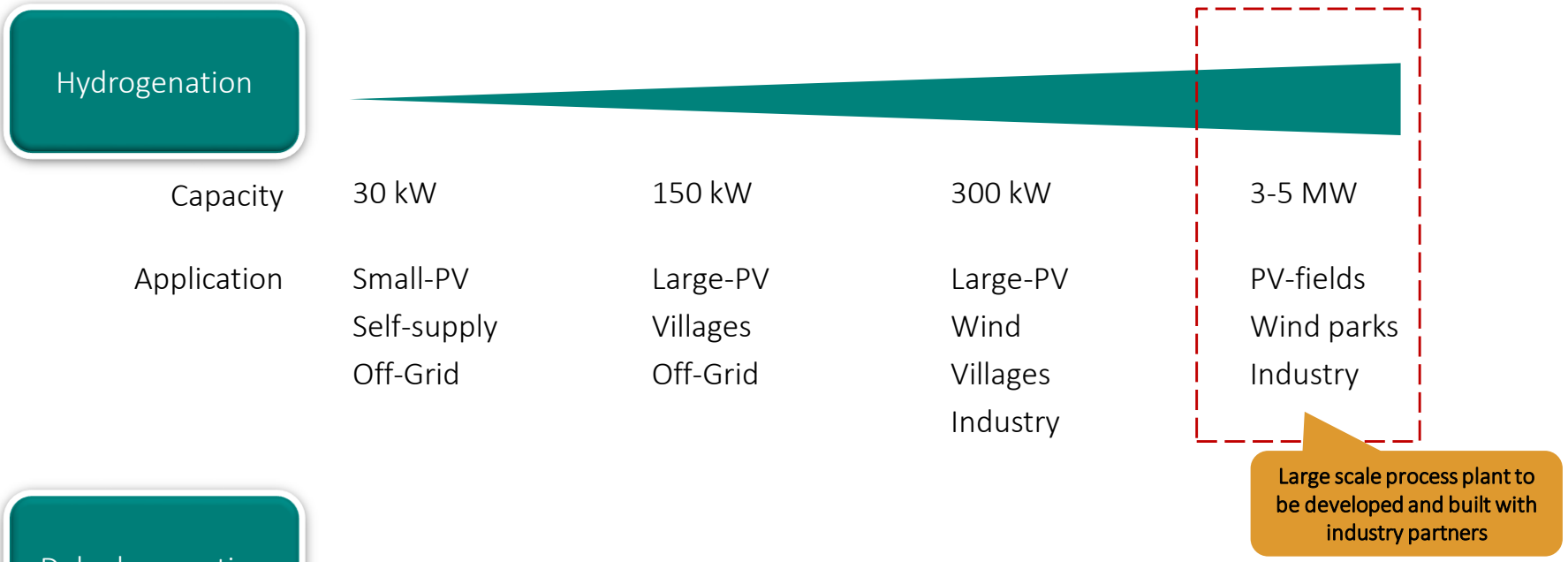
On-grid energy storage

Competing Technology:
Fossil reserve power plants, power reserve, batteries

Business case (2020+)

Self-supply with renew. Energy, grid services, arbitrage

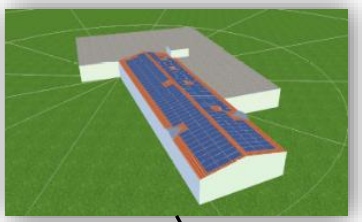
Hydrogenious Technologies‘ range of components allows for a modular setup of complete systems



LOHC Prototype at Hydrogenious Technologies in Erlangen; Germany

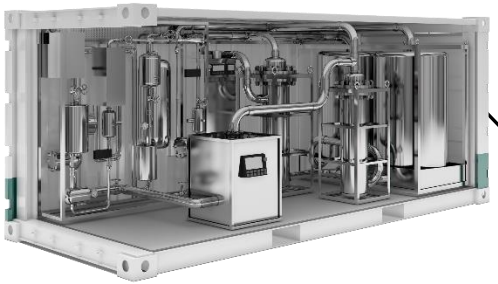
Status: running

Photovoltaics
97 kWp



Swinning School
All-year heat demand

HydroSTORE Demo-System
Hydrogenation
Status: running



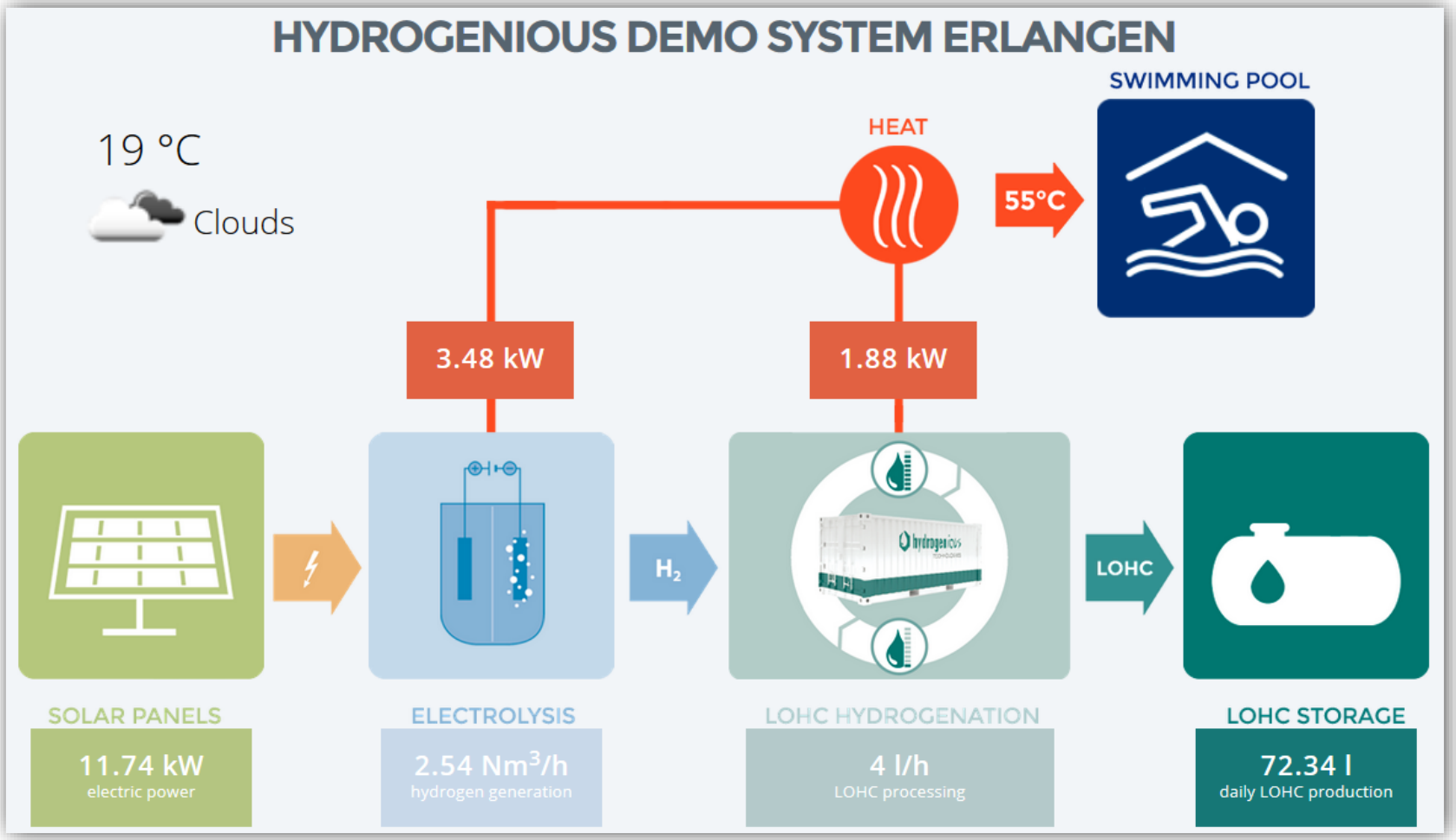
PEM-Electrolysis
Siemens
50-100 kW
Status: running

Purposes:

- Demonstration of LOHC technology on-site
- Continuous improvement through operational experience
- Innovative energy concept to improve energy supply of buildings

LOHC Prototype at Hydrogenious Technologies in Erlangen; Germany

Hydrogenious Live Demo System: www.hydrogenious.net



Thank you for your interest!

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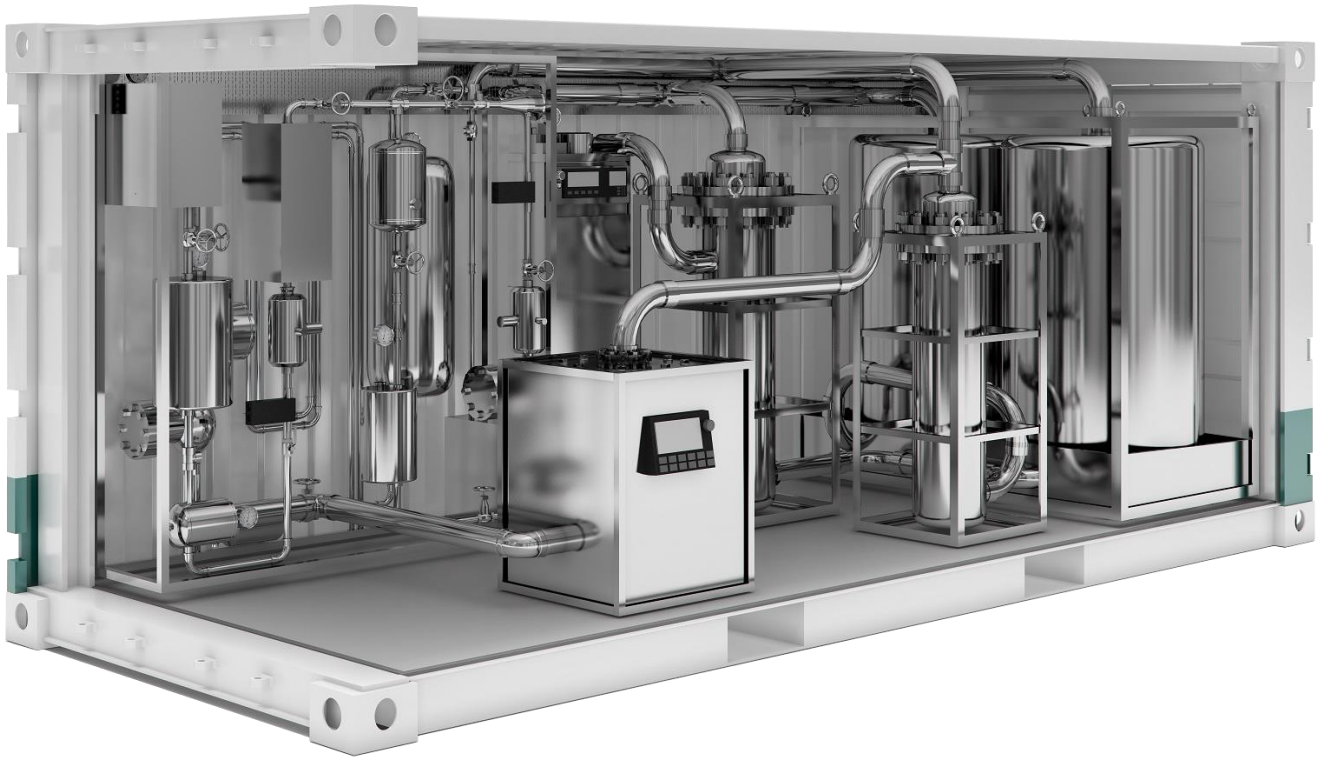
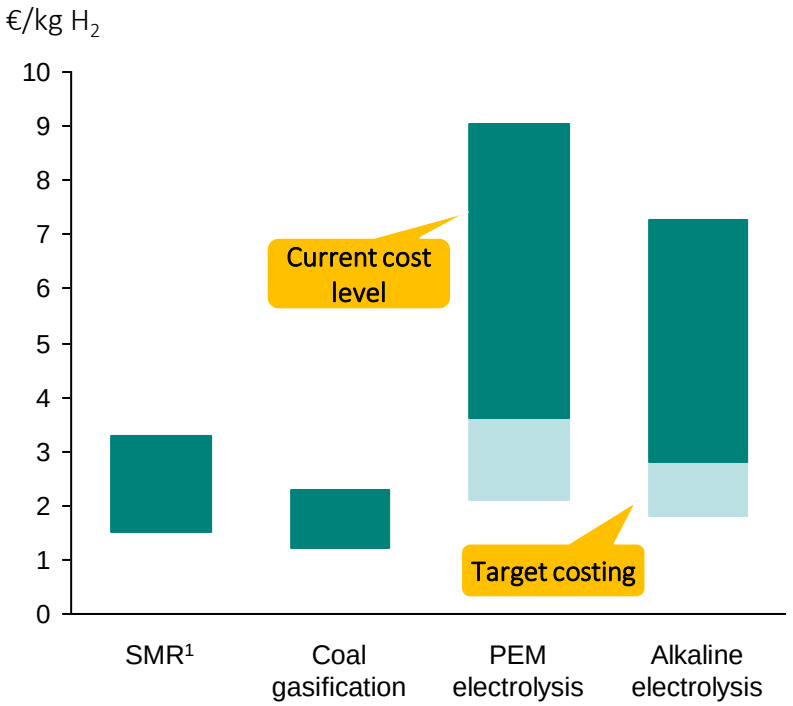


Comparison of different LOHC materials

Parameter		Dibenzyltoluene	N-Ethyl-Carbazole	Toluene
Storage density		2.05 MWh / Nm^3	2.01 MWh/ Nm^3	1.58 MWh / Nm^3
Melting point / boiling point	Loaded	-39°C / 390°C	69,1°C / 348°C	-95°C / 111°C
	Unloaded		/ 280°C	-127°C / 101°C
Hydrogenation	Pressure	30-50 bar	70 bar	10-50 bar
	Temperature (exothermic)	150°C	150°C	50-100°C
Dehydrogenation	Pressure	1 bar	1 bar	3 bar
	Temperature (endothermic)	320°C	220°C	350°C
Toxicity		-		
Flammability		low	low	high
Price		<4 €/kg	>40 $/kg	<1 €/kg

Hydrogen production from fossil fuels still lowest cost production method, but green hydrogen offers large potential

Cost / kg hydrogen comparison across production technologies



- Unit cost of hydrogen production highly dependent on plant size, energy prices and plant utilization
- High investment costs of electrolyzers expected to decrease significantly within coming years
- Average utilization of electrolyzers powered by renewable energies lower than conventional production due to unsteady availability of wind and solar energy

1. Steam methane reforming

Two scenarios were calculated for similar settings to demonstrate LOHC cost advantage over CGH2

Production site

- Large central hydrogen production and storage unit
- Hydrogen storage tanks with storage volume of 150% daily production
- Hydrogen compression up to 200bar (CGH2) / 50 bar (LOHC)

Industrial H_2 production

Logistics

- Supply via trucks and unloading of hydrogen at customer sites
- Assumed costs:
  - € 35 per working hour
  - €1.30 /l Diesel
- Assumed loading and unloading time: 1h for both technologies

Customer site

- Decentral dehydrogenation units at each customer site
- Two scenarios: Average daily hydrogen demand per customer of 180 kg / 500 kg
- Peak demand of 9.1 kg/h / 30 kg/h
- Cost of natural gas: € ct. 3.2 /kWh
- Hydrogen pressure of 50 bar at customer

Industrial utilization

H_2 filling stations

Hydrogenious Technologies‘ portfolio of LOHC systems ranges from 30kW to 1MW

LOHC Energy Storage

SMALL (30 kW)	MEDIUM (300 kW)	LARGE (1 MW)
Electrolysis 30 kW Hydrogenation 15 kW Dehydrogenation Fuel cell Controls Container	Electrolysis 300 kW Hydrogenation 60 kW Dehydrogenation Fuel cell Controls Container	Electrolysis 1 MW Hydrogenation 300 kW Dehydrogenation Fuel cell Controls Container