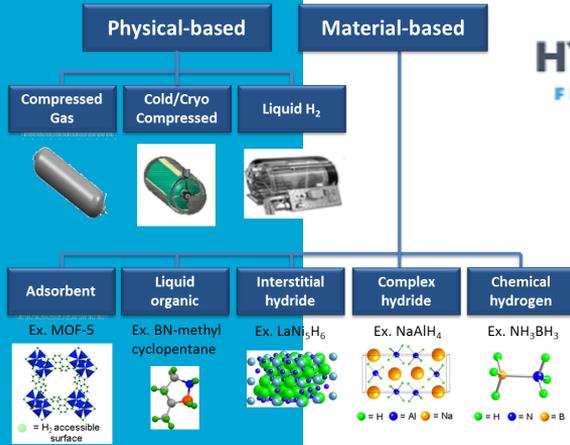


How is hydrogen stored?



MARITIME
HYDROGEN
FLORØ, NORWAY



MARINE
ENERGY
18-19 SEPTEMBER 2019

Interreg
EUROPEAN UNION
North-West Europe
H2SHIPS
European Regional Development Fund

Metal Hydrides in the H2SHIPS project

Maritime Hydrogen and Marine Energy Conference
Floro Norway September 18-19 2019
Klaas Visser TU Delft

k.visser@tudelft.nl

Why metal hydrides as ship hydrogen storage alternative?

- Drivers for Zero emission in the Netherlands
- Which strategy? The hydrogen case
- ***How to store hydrogen safe and with reasonable volumetric energy density?***
- A concept for maritime sodiumborohydride
- The EU Interreg NWE H2SHIPS project
- Other developments in the Netherlands
- The way ahead, future research

Drivers

- Governmental policy: EU and national
- Supply Chain Operators: clean transport
- Ship owners: compliance with (future) rules and regulations (both on greenhouse gas and air quality)
- Industry: innovation and competitive edge
- Society: towards a sustainable environment

NL Government decided to implement a CO₂-tax for CO₂-emissions.

Drivers

Which strategy?

The Hydrogen case

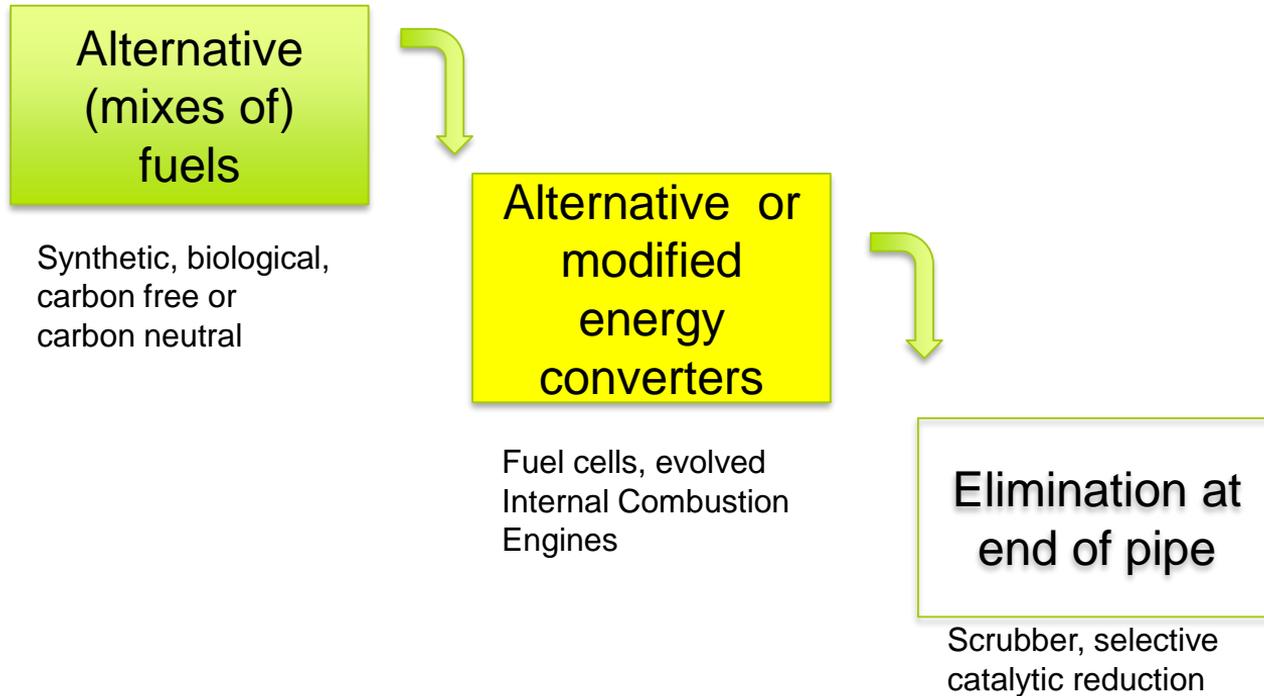
Fuel cells

The on board hydrogen storage challenge

A concept for sodiumborohydride

Topical developments

Which strategy?



Drivers

Which strategy?

The Hydrogen case

Fuel cells

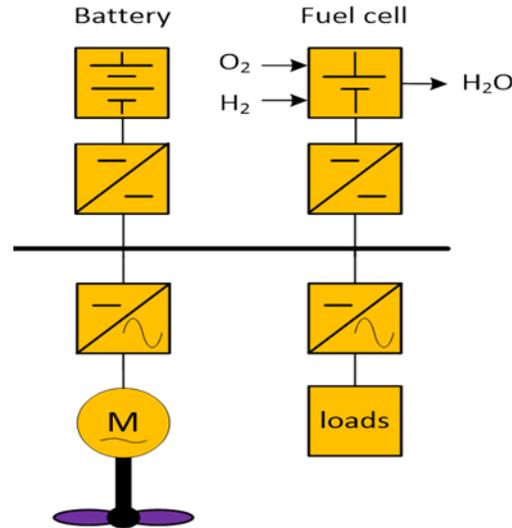
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Topical developments

The Maritime Hydrogen case

No emissions, silent, no single point of failure, graceful degradation, solid state conversion: less maintenance req.



Drivers

Which strategy?

The Hydrogen case

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Topical developments

Fuel cells characteristics

	LT-PEMFC	HT-PEMFC	SOFC
<i>Operating temperature (°C)</i>	40 - 80	150 - 180	500-1000
<i>Electrical efficiency (LHV)</i>	50-60	40-45	50-65
<i>Fuel purity required</i>	99.999% H ₂	CO<3%	Light hydrocarbons (S<20 ppm)
<i>Gravimetric power density (W/kg)</i>	250-1000	-	8.0-80
<i>Volumetric power density (W/l)</i>	300-1550	-	4.0-32
<i>Life time</i>	5 to 20k hours	10 to 60k hours	10 to 40k hours
<i>Start-up time</i>	<10 seconds	10 to 60 minutes	30 minutes to hours
<i>Load transients (0 to 100%)</i>	<5 seconds	2-5 minutes	<15 minutes
<i>Capital cost today (\$/kW)</i>	>1000	4000-4500	3500-15000
<i>Technology Readiness Level (TRL)</i>	8	7-8	5-7
<i>Cooling</i>	Water cooling	Water cooling	Air cooling
<i>Waste heat recovery</i>	-	-/+	++

van Biert, L., Godjevac, M., Visser, K., & Aravind, P. V. (2016). A review of fuel cell systems for maritime applications. *Journal of Power Sources*, 327(X), 345–364. <https://doi.org/10.1016/j.jpowsour.2016.07.007>



Fuel cells

- PEMFC: low temperatures, available, high power density, quick start-up, good dynamic performance, pure H₂ required, limited waste heat recovery, TRL: 7-9
- SOFC: high temperatures, high efficiency, high cost, low power density, higher tolerance to non H₂-fuels, useful waste heat recovery, TRL: 5-7
- Additional maritime aspects: low noise, no CO₂, no NO_x, no SO_x, no particulate matters. solid state tech: low maintenance (cost), high reliability and graceful degradation when in modules and stacks.

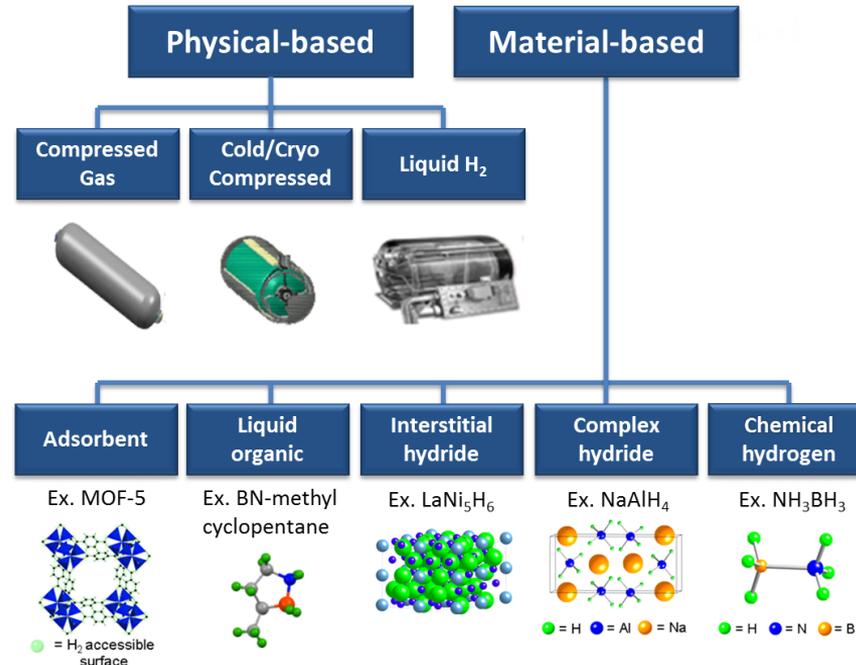
[1] Vora, S. D., Lundberg, W. L., & Pierre, J. F. (2017). Overview of U.S. Department of Energy Office of Fossil Energy's Solid Oxide Fuel Cell Program. *ECS Transactions*, 78(1), 3–19. <https://doi.org/10.1149/07801.0003ecst>

[2] Mittermeier, T., Weiß, A., Hasché, F., Hübner, G., & Gasteiger, H. A. (2017). PEM Fuel Cell Start-up/Shut-down Losses vs Temperature for Non-Graphitized and Graphitized Cathode Carbon Supports. *Journal of The Electrochemical Society*, 164(2), F127–F137. <https://doi.org/10.1149/2.1061702jes>

[3] van Biert, L., Godjevac, M., Visser, K., & Aravind, P. V. (2016). A review of fuel cell systems for maritime applications. *Journal of Power Sources*, 327(X), 345–364. <https://doi.org/10.1016/j.jpowsour.2016.07.007>

The on board hydrogen storage challenge

How is hydrogen stored?



Source: hydrogenandfuelcells.energy.gov

Drivers

Which strategy?

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Topical developments

Some concerns from our concept blue paper:

Liquefied hydrogen

- Release of LH2 into enclosed spaces
 - Pressure build-up due to rapid vaporization
 - Low temperature effect on equipment
 - Ignition of "oxygen snow" in LH2
- Loss of vacuum in cryogenic storage tanks
 - Excessive Boil-off discharge/pressure build-up in tank
- Sloshing in tank
 - Loss of tank pressure
- Inerting issues
 - Condensation and solidification of nitrogen
- Condensation and solidification of oxygen
- Safe arrangement of Tank connection space

Compressed hydrogen

- Release of CH₂
- Pressure
- Ignition mechanisms
- The high pressure is a hazard on its own

Common concerns for LH₂ and CH₂

- Develop relevant hazardous (EX) zones for hydrogen
- Ignition source control
- Material embrittlement
- Risk of autoignition when burst discs are used
- Capacity of safety relief valves
- Ignition of hydrogen in case of release through the vent mast
- Use of inerted spaces to reduce explosion risks
 - Asphyxiation hazard
 - Limits accessibility

Drivers

Which strategy?

The Hydrogen case

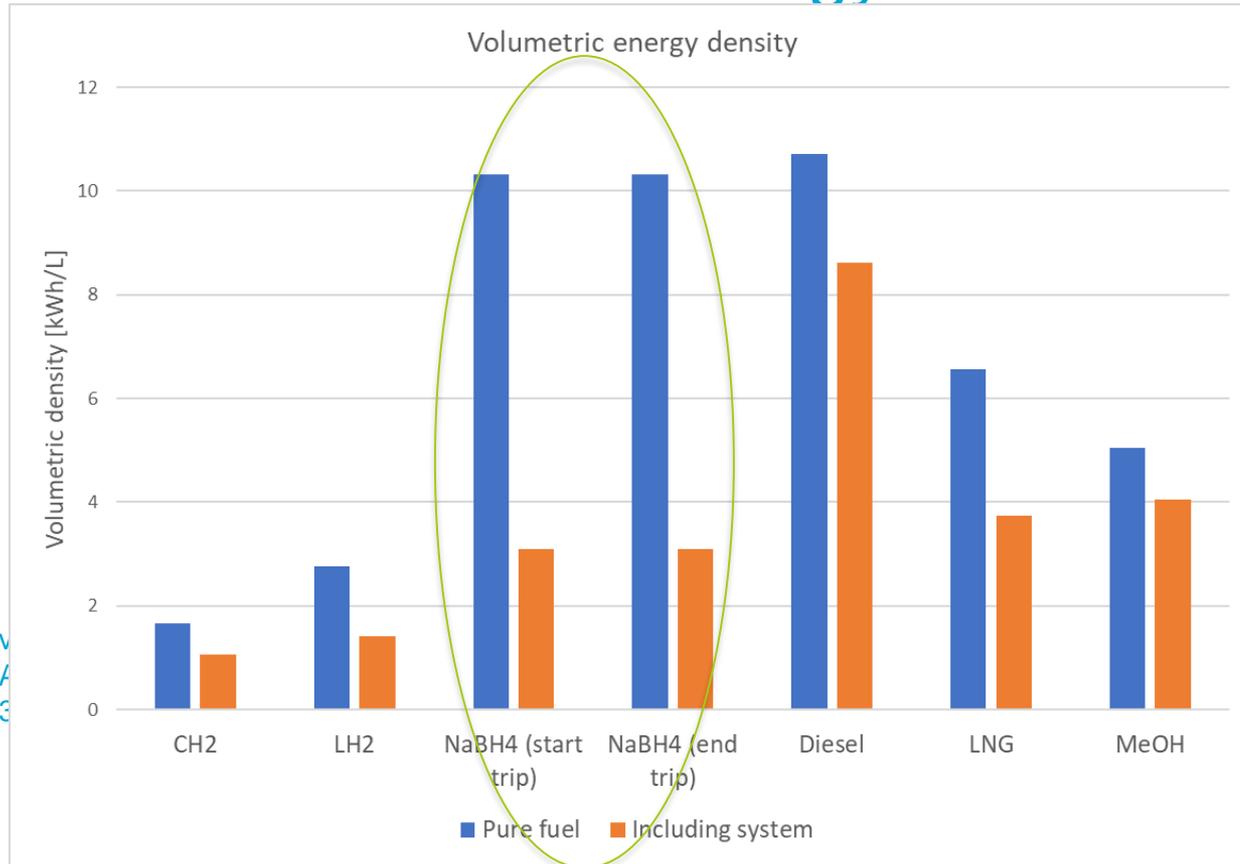
Fuel cells

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Topical developments

Volumetric Energy densities



Drivers

Which strategy?

The Hydrogen case

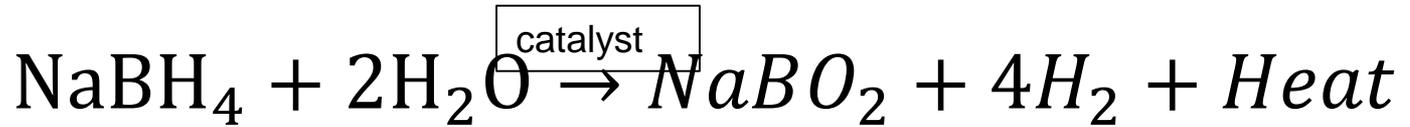
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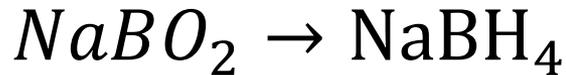
Topical developments

Principle of NaBH₄ as a H₂ carrier



1 kg H₂ = 141,7 MJ or 39,4 kWh before the engine (Fuel Cell)

Regeneration of the spent fuel



Source: *H2Fuel*

Drivers

Which strategy?

The Hydrogen case

Fuel cells

The on board
hydrogen storage
challenge

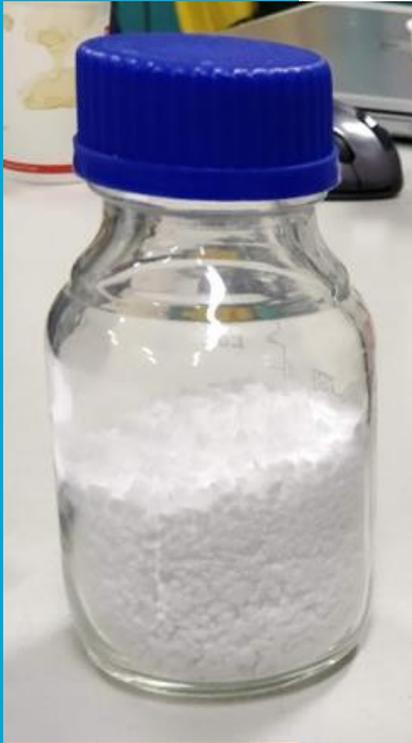
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Topical developments

NaBH₄ characteristics

- characteristics:

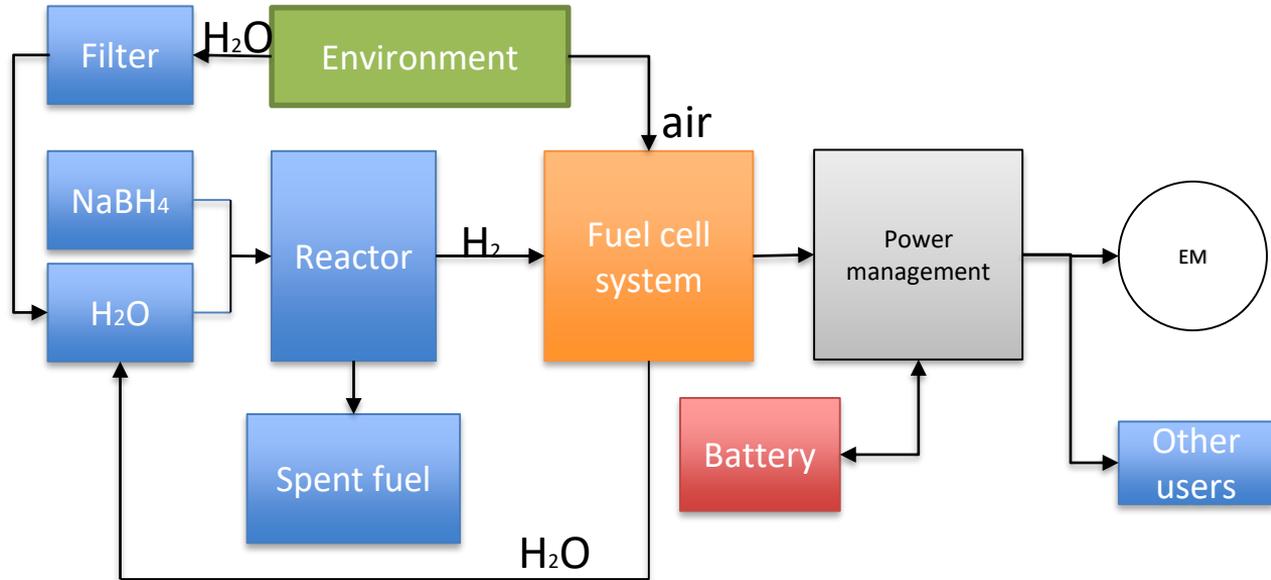
- Metal hydride supplied in powder, granules or in a solution
- Reacts with water
- Flammable, but very slow
- Energy density (38,5 MJ/kg)
- Can be stored in a solution with a stabilizer (eg. *NaOH*)



Molecular Formula	<i>BH₄Na</i>	
Description	White crystal powder	
Mol mass	37.83	g/mol
Melting point	400	°C
Boiling point	500	°C
Density	1.035	g/mL at 25 °C
Flashing point	70	°C
Water solubility	550	g/L at 25 °C
ΔH	-188.6	KJ/mol
ΔG	-123.9	KJ/mol
$^{\circ}S$	101.3	J/mol/K
C_p	86.8	J/mol/K

Source: H₂Fuel-Systems B. V.

A concept for maritime Sodiumborohydrid



Drivers

Which strategy?

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Proof of Concept in Rotterdam

Drivers

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Courtesy: H2Fuel-Systems B.V.

What are the urgent maritime storage challenges?

- a. hyperbaric 350-700 bar? Certification complex, lower density, high TRL, logistic availability gas in ports?
- b. liquid (-253 degrees Celsius)? Certification very complex, high TRL, low density, lesser support of captains?, logistic availability liquefied in ports?
- c. chemical storage in molecules: CH₃OH, CH₄, NH₃? Not directly applicable for PEMFC (reforming required), logistic availability better, methanol liquid in ambient conditions, certification LNG complex, CO₂ as exhaust gas?
- d. chemical storage in chemical hydrides: NaBH₄? Experimental, proof of concept performed, certification process much less complicated?, potential higher storage density, new logistical process with solid states and spent fuel disposal/regeneration, regeneration process needs update technology for higher scale and efficiency..

Drivers

Which strategy?

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Topical developments

Implementation as part of the H2SHIPS INTERREG project

Helping H2 become a widespread solution for shipping in NWE

From the



to the



- Sub- objectives:
 - Determine appropriate technology
 - Develop favorable regulatory framework
 - Help creating a market

Drivers

Which strategy?

The Hydrogen case

Fuel cells

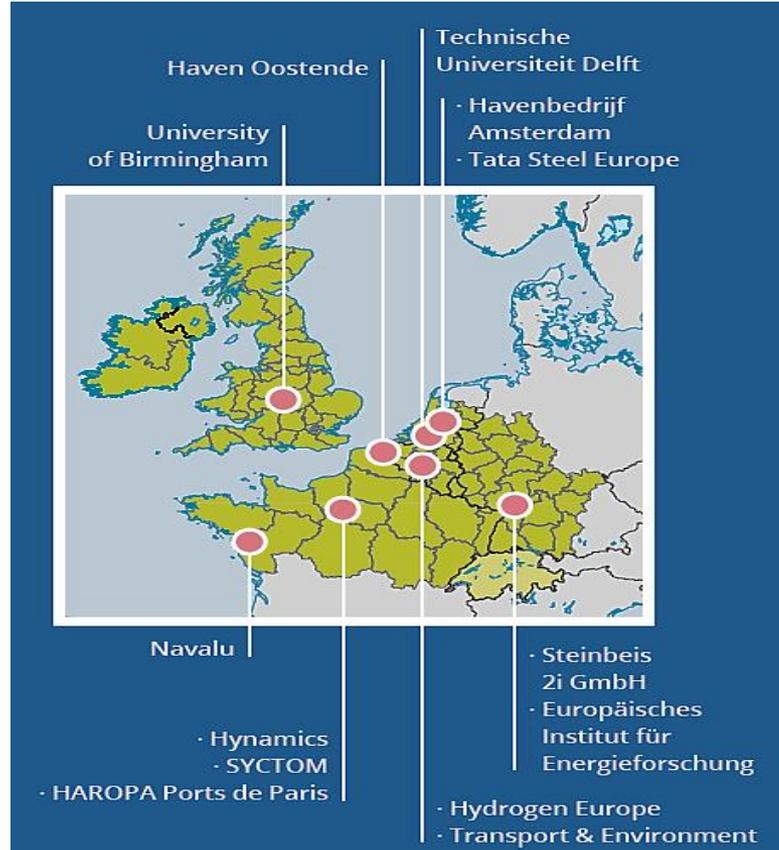
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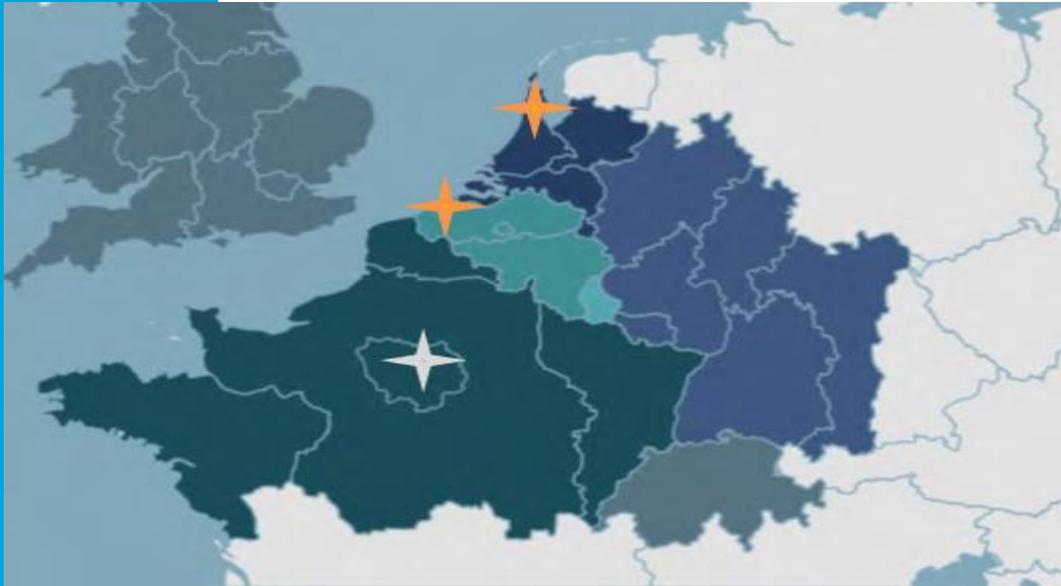
Topical developments



+ 2 Sub-partners
 + 15 Associated Partners



3 ports 3 core areas



- USAGE: *Amsterdam*
H2 system on
newbuilt ship
- LOGISTICS:
Oostende
Bunkering
solutions
- PRODUCTION: *Paris*
Local electrolysis

Budget and Timeline

Total budget: 6,3 M€

ERDF funding: 3,5 M€

Total project duration: 3,5 years

- **1st reports on regulatory frameworks: Apr. 2021**

- **Complete roadmap: Apr. 2022**

- **1st things to see in Ostend and Amsterdam
End of 2020**

Drivers

Which strategy?

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Topical developments

The Amsterdam Demonstrator in H2SHIPS

The NL demo will take place on a new Port Authority Vessel of Port of Amsterdam. The vessel will have a zero emission propulsion and will sail in the Amsterdam urban and port area.

- The configuration will be battery-electric, with a maritime fuel cell as range extender and sodiumborohydrid as hydrogen carrier.
- NL partners: Port of Amsterdam, Tata Steel and Delft University of Technology.
- **Port of Amsterdam and TATA find it very important, that existing small inland ships with small destinations at the end of inland waterway logistical lines towards the Netherlands, Belgium and France can be sustained by a retrofit modification of zero-emission propulsion power. This demo enables this process.**

Drivers

Which strategy?

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Topical developments

Amsterdam Demo Design Data

Drivers

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Dimensions:

Max length: 20 meters

Max. beam: 4.25 meters

Max. draft: 1.50 meters

Max height above waterline: 1.90 meters

Accommodation: 25 persons.

Operational profile and propulsion data:

-the requirement to sail with an average speed of **12.5 km/h** (3.5 m/sec) for a period of **10 hours**

-propeller power: 220 hp (162 kW), expected for this vessel a maximum of **200 kW**

-Electrical power should facilitate operation of a bow thruster and a stern thruster (bot not at full speed) and the heating of the ship.

-Storage of hydrogen in a metal hydride

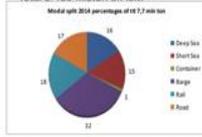


Map Courtesy Waternet Amsterdam

Future plan

Location

- Regio 1: NL, Moerdijk en omgeving (475 kt)
- Regio 2: ARA havens en België (Evergem en Ghlin) (427 kton)
- Regio 3: Maastricht en Ivoz Ramet (B.Segal) (1.076 kton)
- Regio 4: Duitsland, Ruhr gebied (134 kiloton) - Region 5: Zwitserland, Bazel (45 kton)
- Regio 6: rivier Moezel (F) (27 kton)
- Regio 7: Paris en omgeving (180 kt)
- Regio 8: Donau (45 kton)
- Total 2.409 kiloton ex IJM



(exclusief retour staal en grondstoffen van ca 500 kton)



- Small inland ship
- 2 propeller shafts, 250 kW, 1 H₂-electric, 1 conventional
- Retrofit of existing ship, commercial cargo test
- Modular hydrogen power pack with Sodiumborohydrid fuel and PEM fuel cells

4

Drivers

Which strategy?

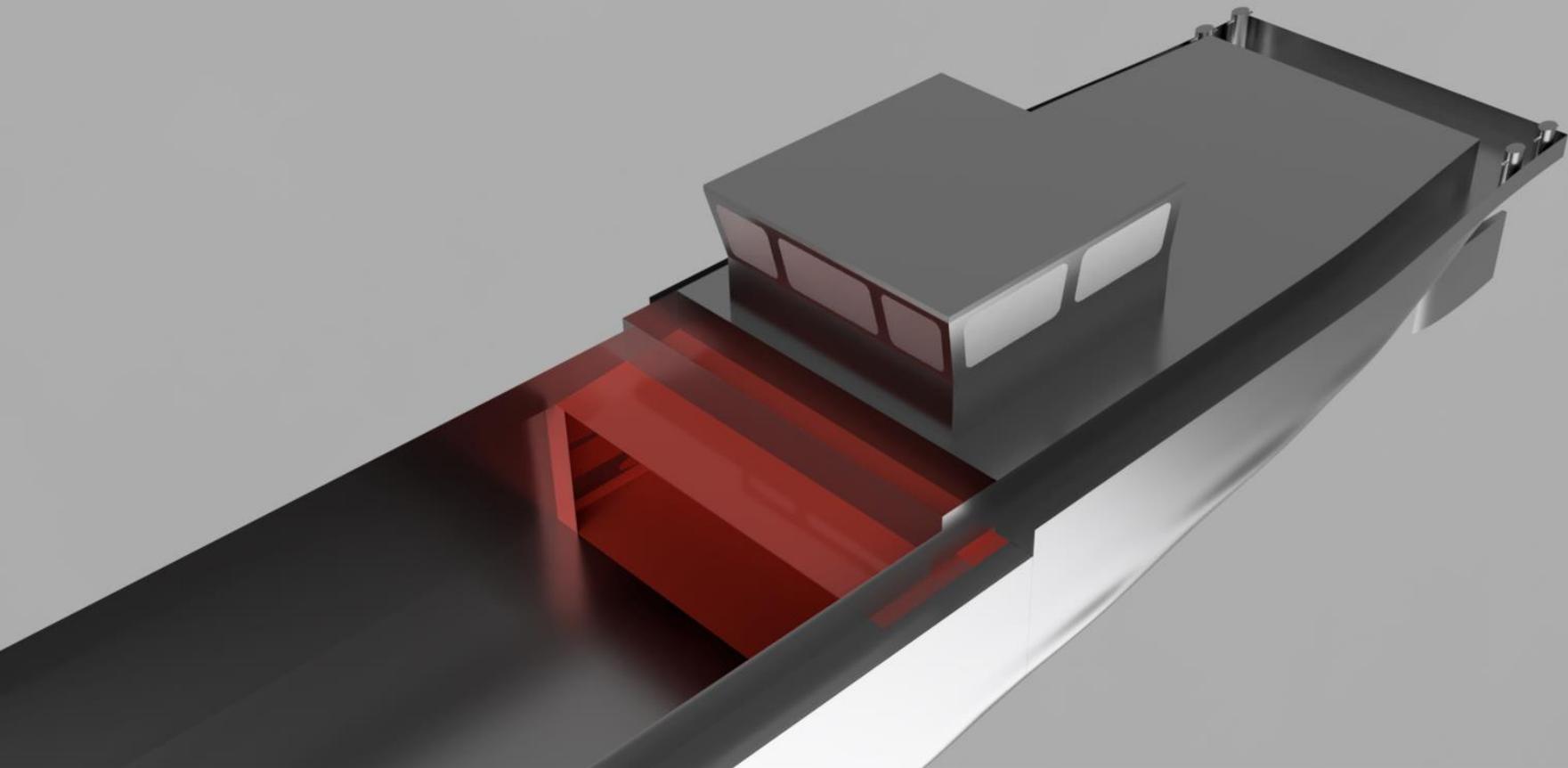
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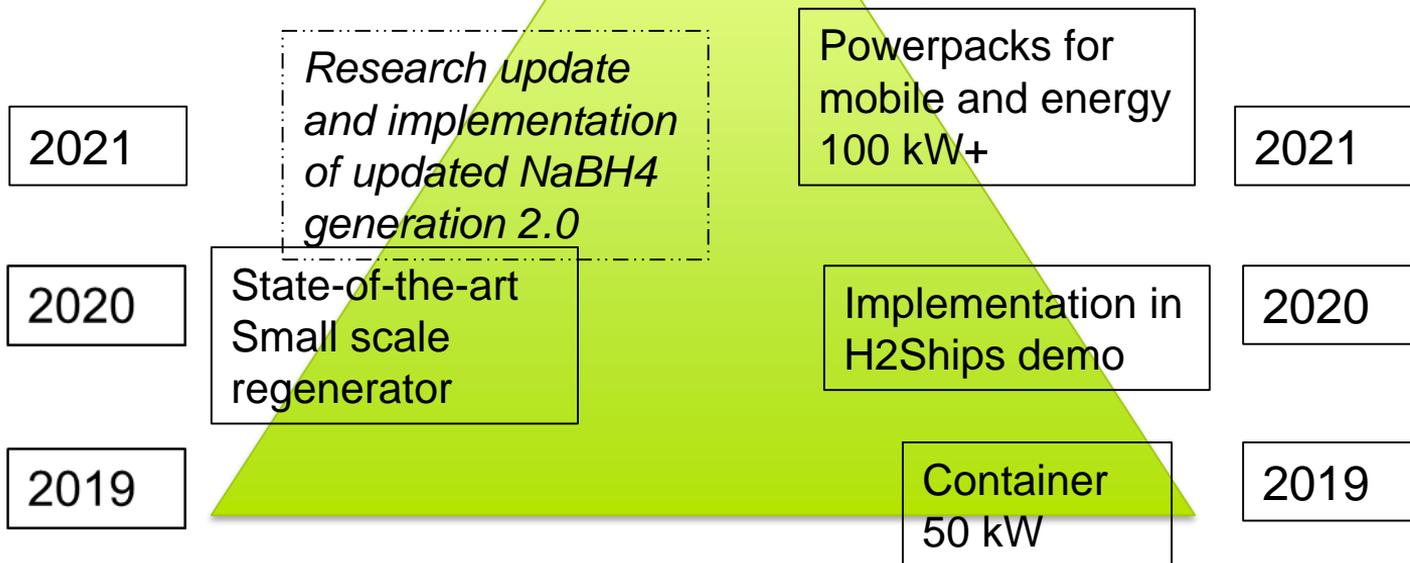
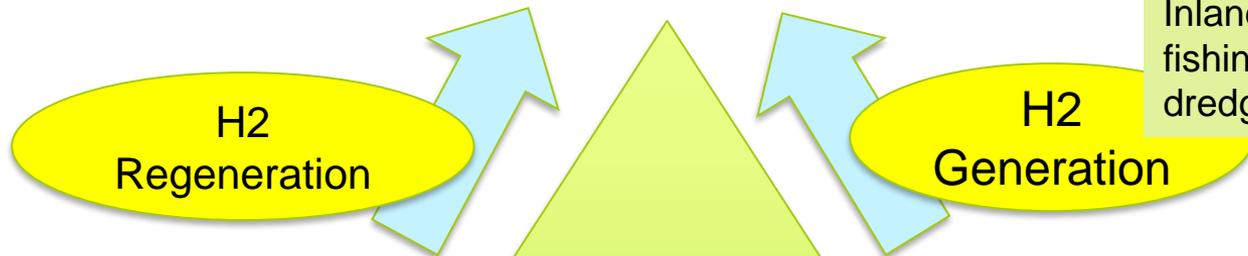
Topical developments



250 kW PEM. 5 cum NaBH₄ for operation of 70+ hours

Way ahead for NaBH₄-as-a-fuel

Present interest:
Inland vessels,
fishing vessels,
dredging, ferries



Drivers

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Thank you! k.visser@tudelft.nl

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