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Solid State Hydrogen Storage: Materials, Integration and Applications

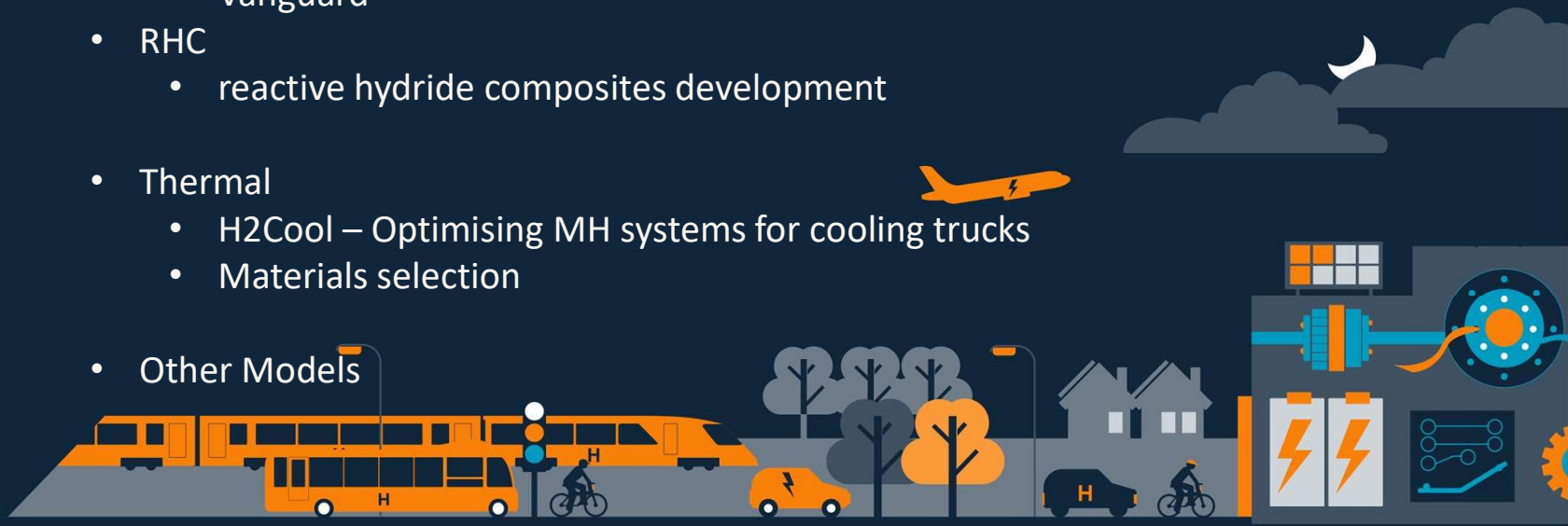
David Grant



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Topics

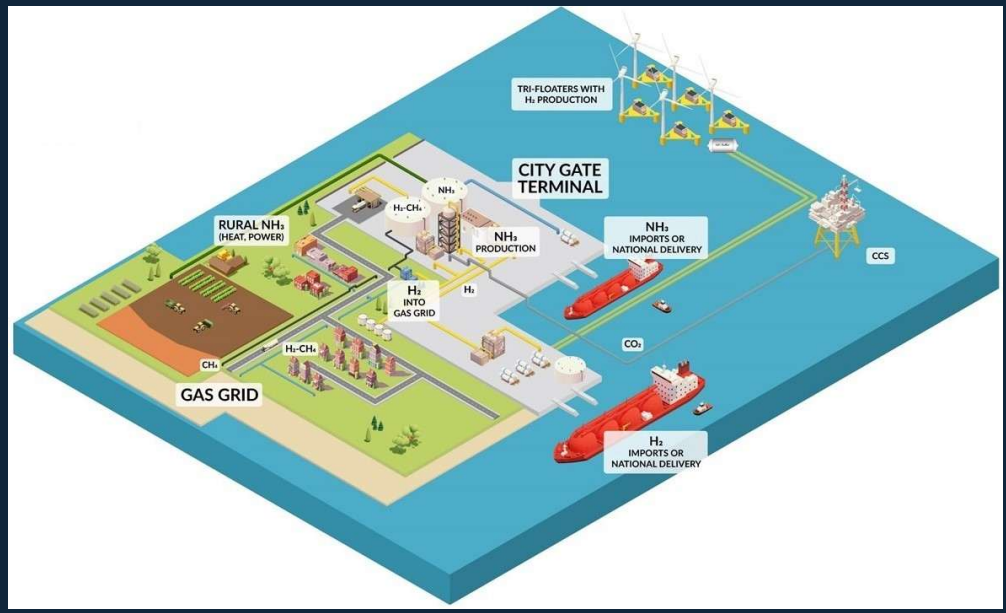
- Stationary applications
  - Offshore - OceanRefuel
  - Modelling and materials selection for high pressure MH compressors
- Marine
  - MariNH_3
  - MH ammonia systems
  - Practical store configuration
- Rail
  - Vanguard
- RHC
  - reactive hydride composites development
- Thermal
  - H2Cool – Optimising MH systems for cooling trucks
  - Materials selection
- Other Models



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Stationary applications

Ocean-REFuel

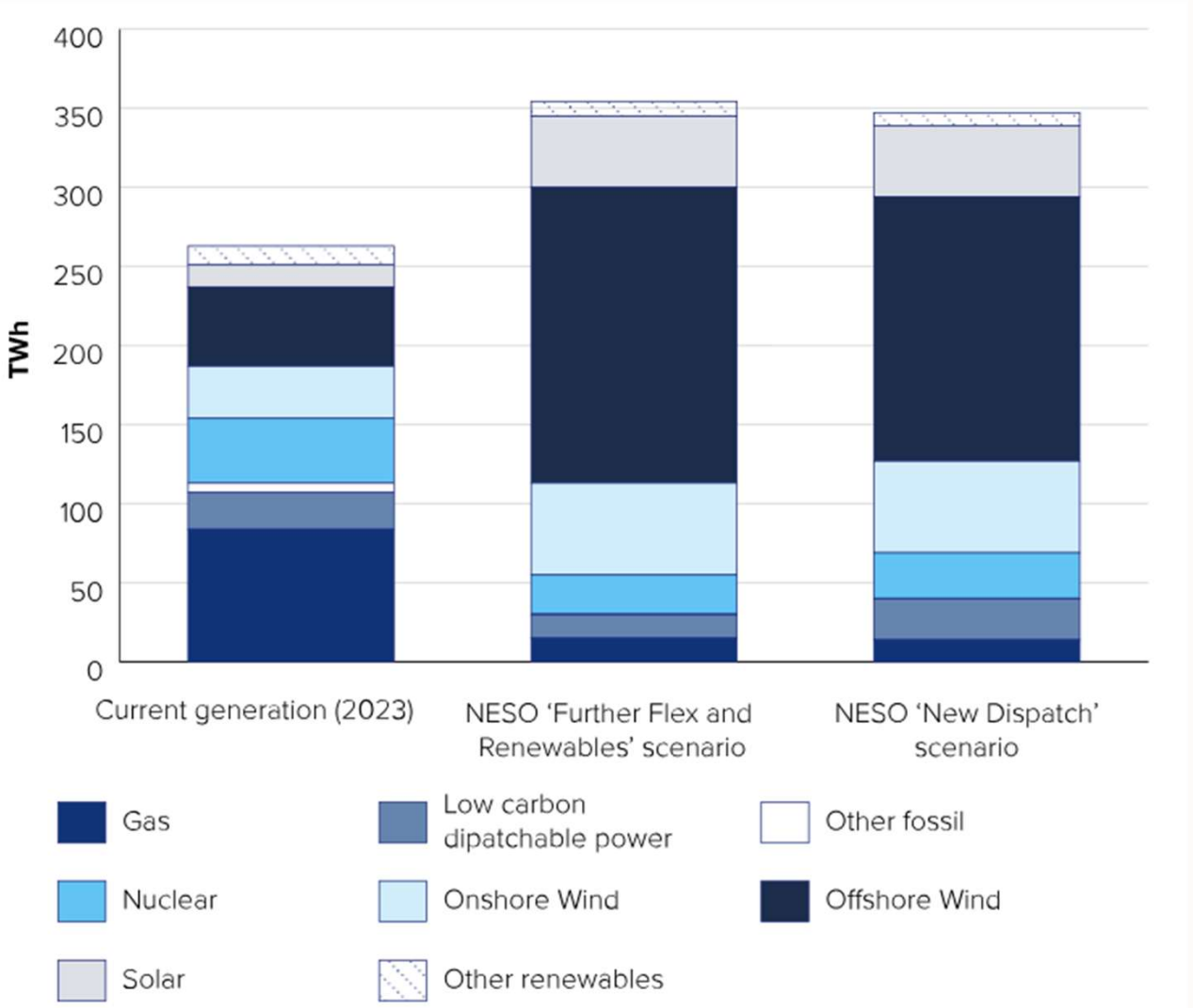


Marcus Adams, Amelia-Rose Edgley, Ramas Al Qudah, Alastair Stuart, David Grant

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NESO
National Energy System Operator

UK Generation in 2030 in the NESO 'Further Flex and Renewables' and 'New Dispatch' scenarios, compared to current generation (TWh)



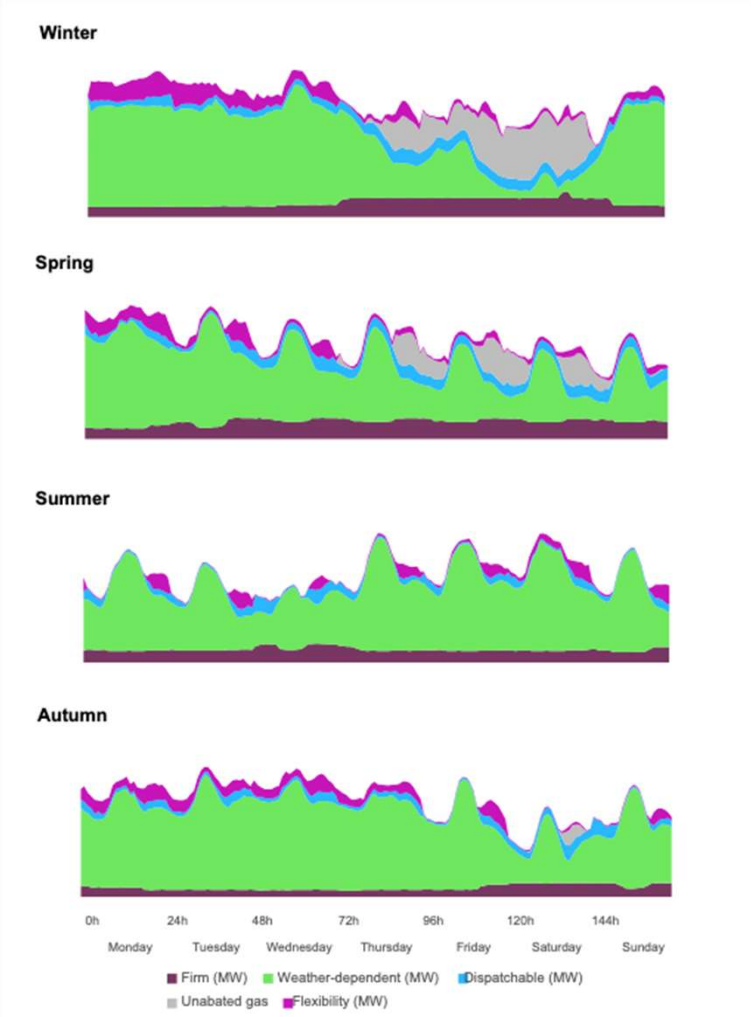
https://www.gov.uk/government/publications/clean-power-2030-action-plan/clean-power-2030-action-plan-a-new-era-of-clean-electricity-main-report

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Dispatchable power requirement (NESO report)

NESO National Energy System Operator

Fuel / technology type (GW)		2023	2030 Further Flex and Renewables	2030 New Dispatch
Variable	Offshore Wind	14.7	50.6	43.1
	Onshore Wind	13.7	27.3	27.3
	Solar	15.1	47.4	47.4
Firm	Nuclear	6.1	3.5	4.1
Dispatchable	Biomass/BECCS	4.3	4.0	3.8
	Gas CCS/Hydrogen	0	0.3	2.7
	Unabated gas	37.4	35.0	35.0
Flexibility	LDES	2.8	7.9	4.6
	Batteries	4.7	27.4	22.6
	Interconnectors	8.4	12.5	12.5
	Demand-side flexibility (excl. storage heaters)	2.5	11.7	10.4
Annual demand (TWh)		**258**	**287**	**287**



https://www.neso.energy/document/346651

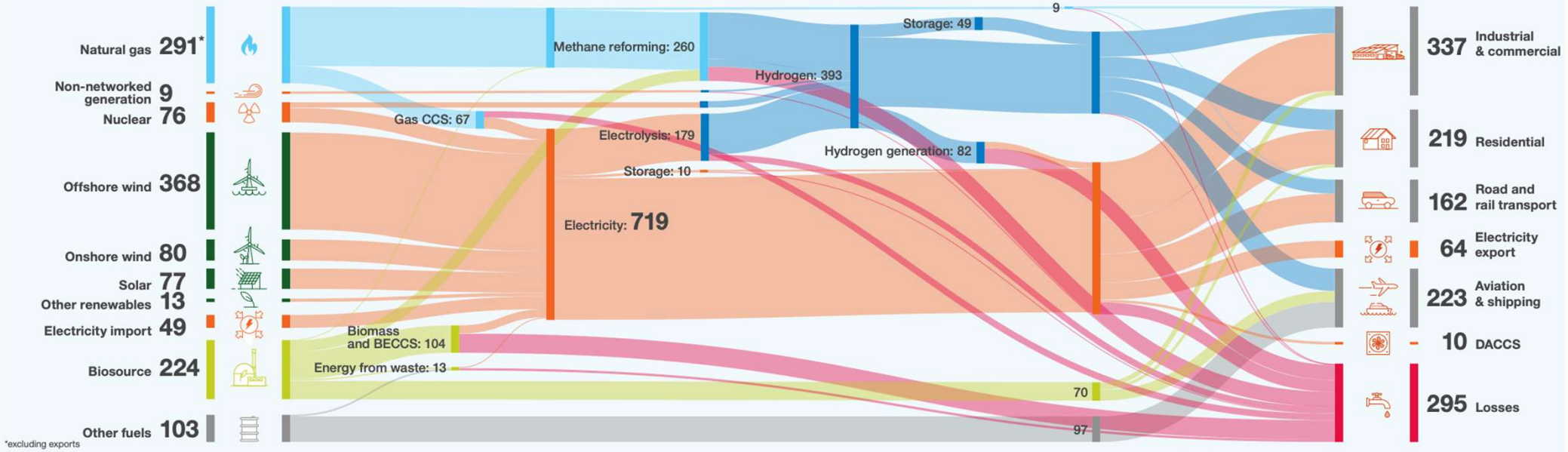
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By 2050 require 49 TWh Hydrogen storage

Hydrogen Evolution

Hydrogen supplies 30% of overall energy needed in 2050 used across all sectors. Overall energy demand drops by 414 TWh driven primarily by the remaining demand that is electrified. Natural gas is still used for electricity and hydrogen production in 2050 but it is abated through CCS.

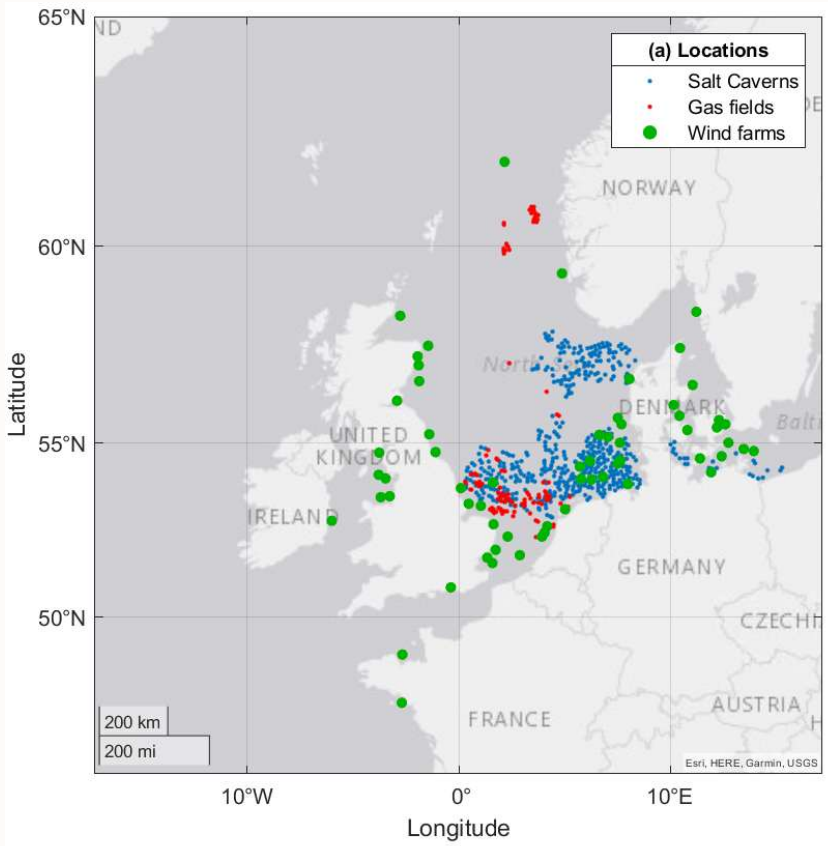
Total energy supply
1292 TWh

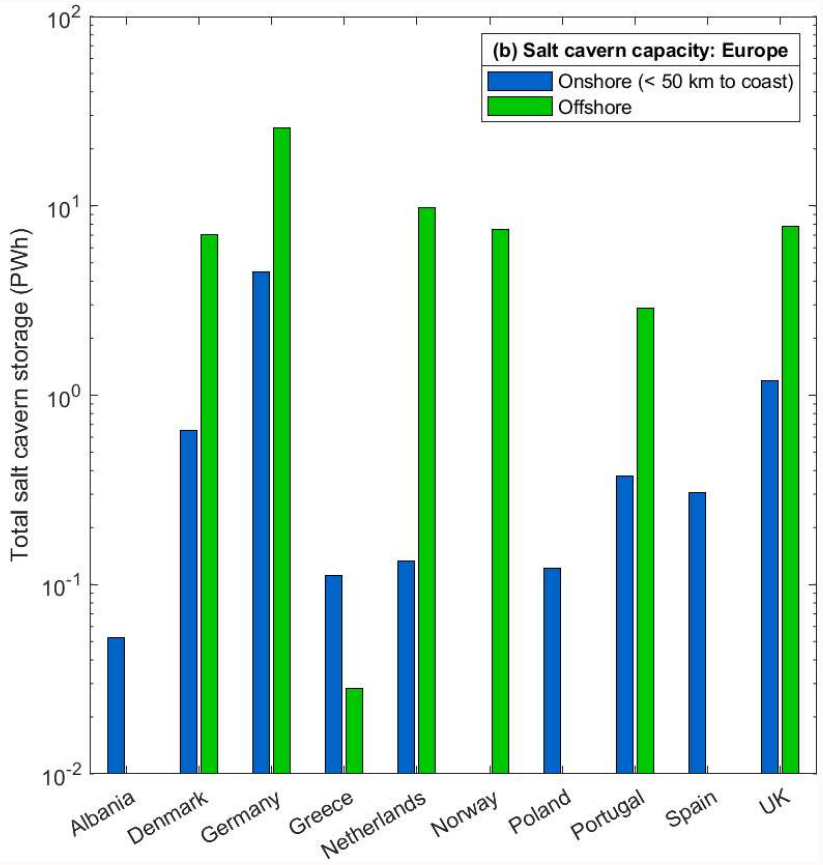


NESO Future Energy Scenarios, July 2024

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Underground hydrogen storage - viable method to store hydrogen at the TWh scale

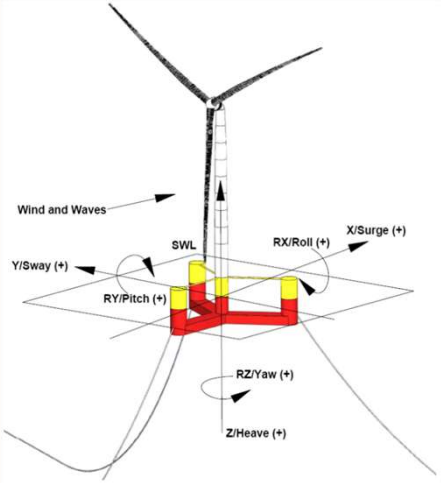




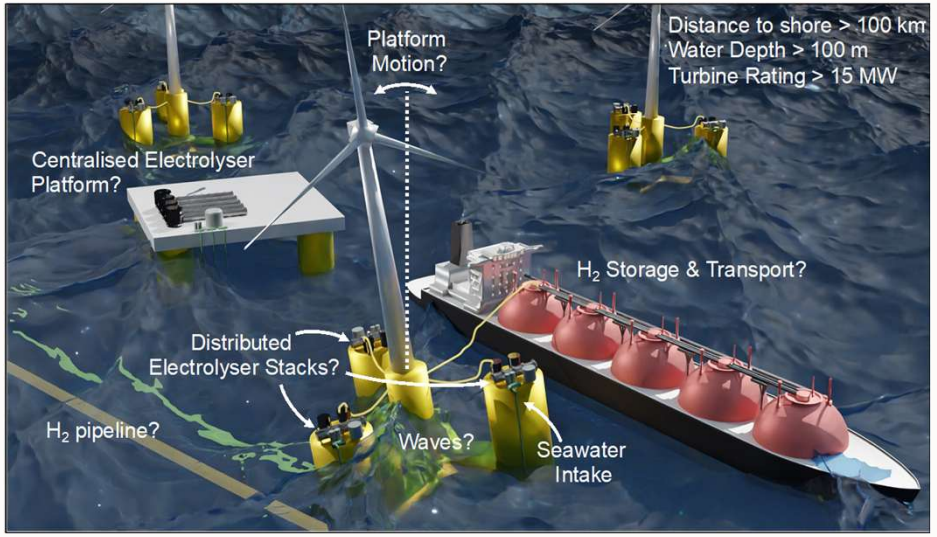
From electricity to Hydrogen (offshore)

Ocean-REFuel

IEA **15MW** Floating Wind Turbine



Electrolyser: 12 MW TOT. →8 x 1.5MW



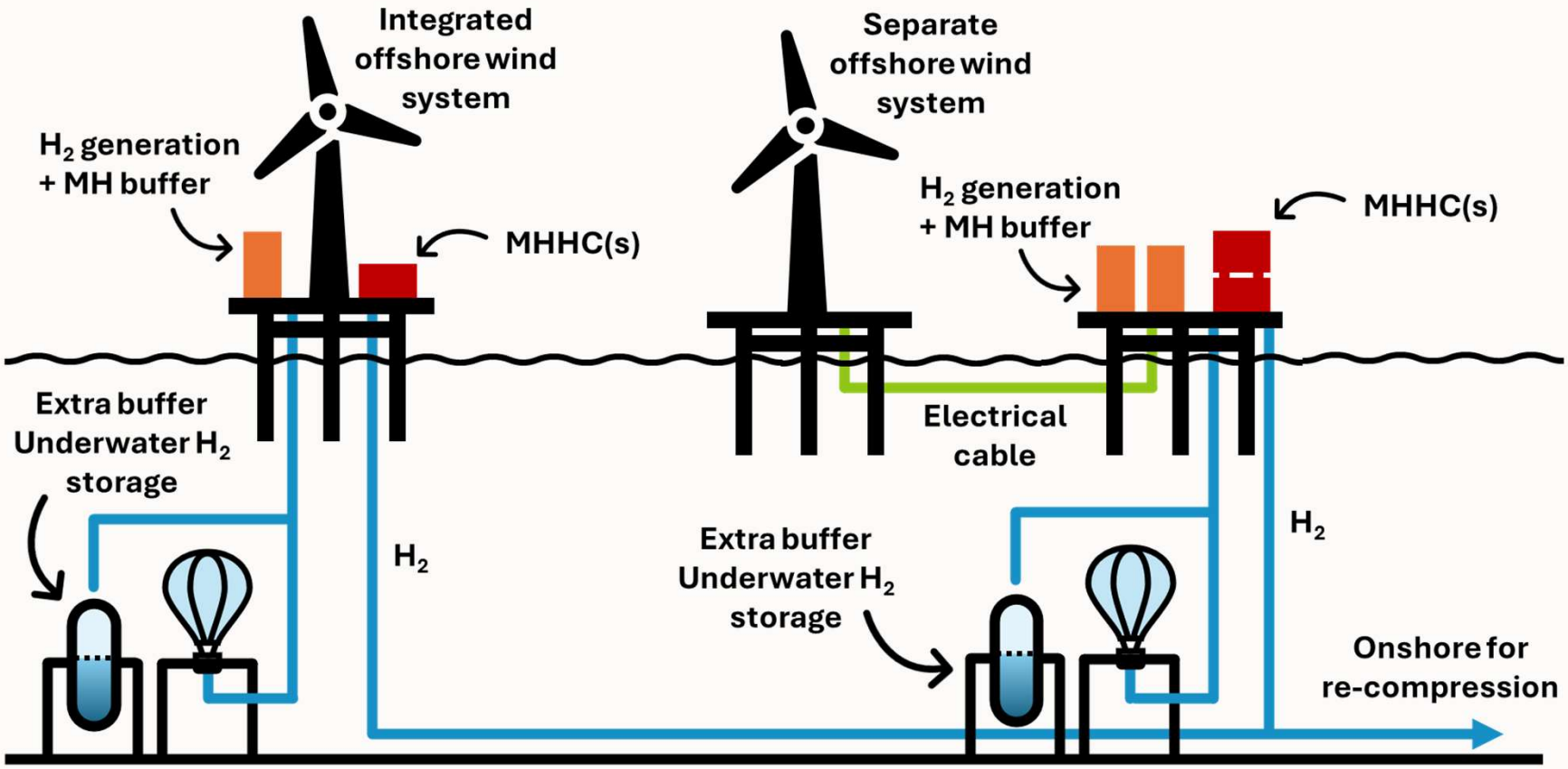
- Capacity factor of 64%
- AWE @ £800/kW, Lifetime 30,000h operation, CAPEX 57% of H_2 cost
- 1h per start-up/shut down cycle
- 366 on/ off cycles per year
- 75-80% utlisation of annual energy generated
- Stack minimum load of 250kW (ca. 15% of 1.5MW)

H_2 1100 tH2 / y / platform
@ 56kWh/kgH_2
@<£4.5/kgH_2

UKRI Engineering and Physical Sciences Research Council
Cardiff University Prifysgol Caerdydd
Imperial College London
Newcastle University
University of Nottingham UK | CHINA | MALAYSIA
University of Strathclyde Glasgow

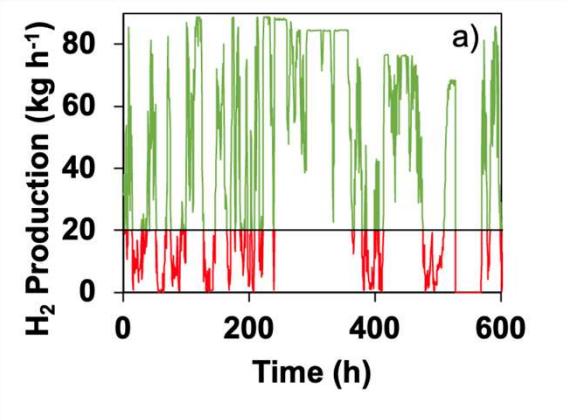
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Offshore metal hydride buffer store and compressor



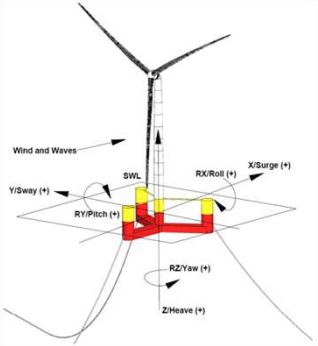
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Slides on buffer tank sizing

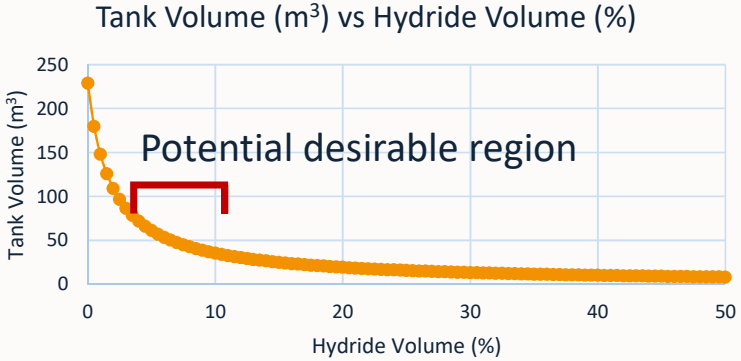


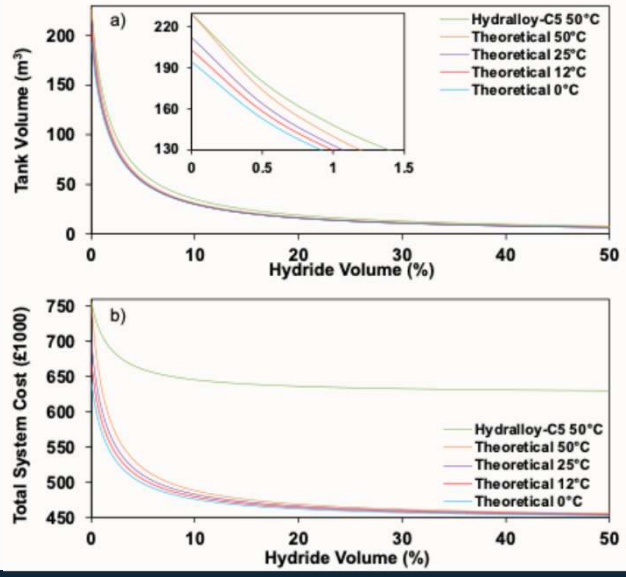
Snapshot metered power output (MWh) for a single offshore wind farm in 2023.
European Offshore Wind Deployment Centre in Aberdeenshire consisting of 11 x 8.8 MW turbines

IEA 15 MW Floating Wind Turbine
With 12 MW Electrolyser



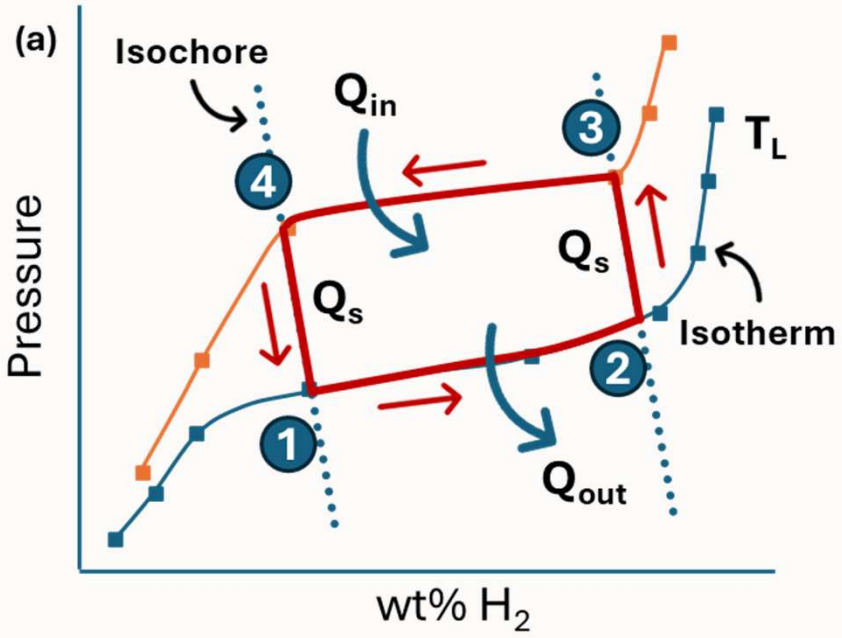
250 kg Hydrogen tank

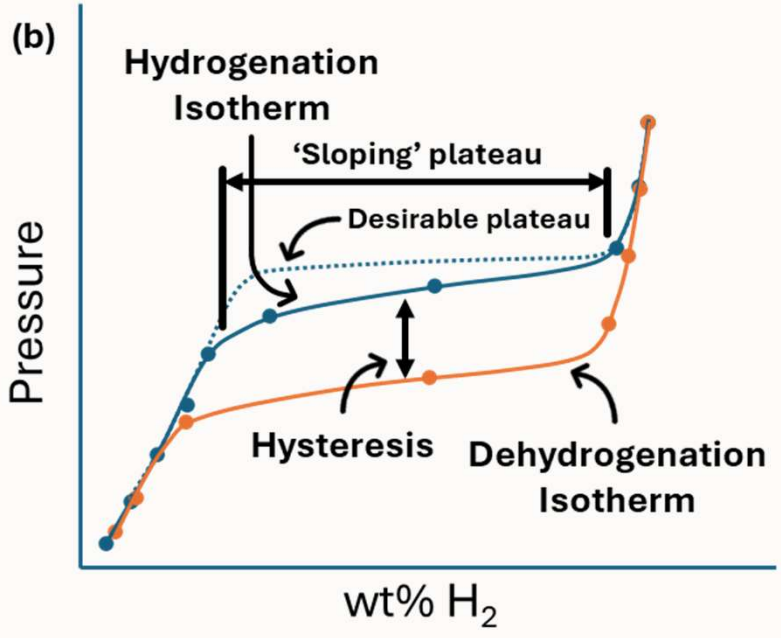




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Buffer stores - ensure a steady flow of hydrogen to the compressor from electrolyser

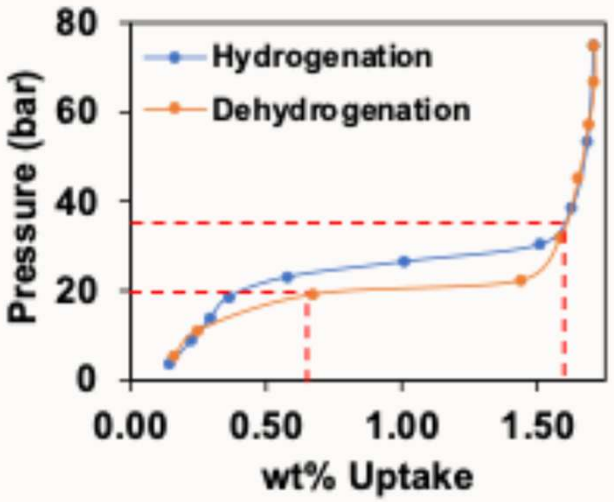




Constraint: Input pressure from electrolyser typically 35 bar, Output pressure to compressor 20 bar operating at system temperatures

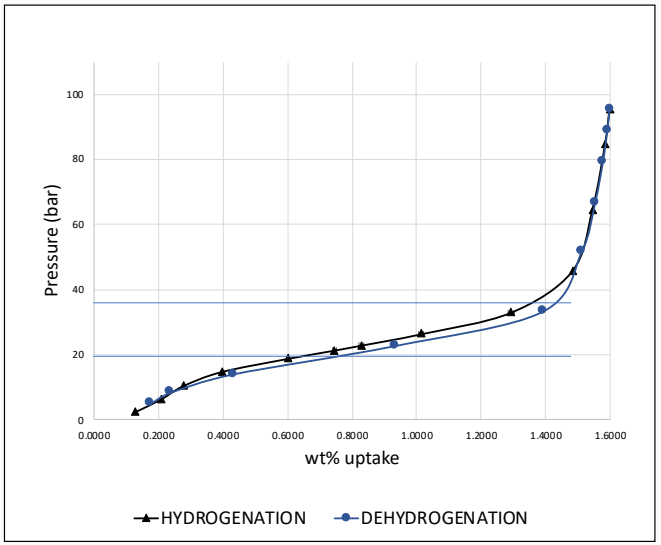
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Flat plateau and/or minimal hysteresis to maximise usable stored hydrogen



PCI for Hydralloy-C5 at 50 °C

Example 250 kg hydrogen buffer store	Steel Tank	Hybrid (Tank + 7vol% Hydride) Hydride at £25/kg
Volume/m^3	229	47
Cost/£	750k	510k

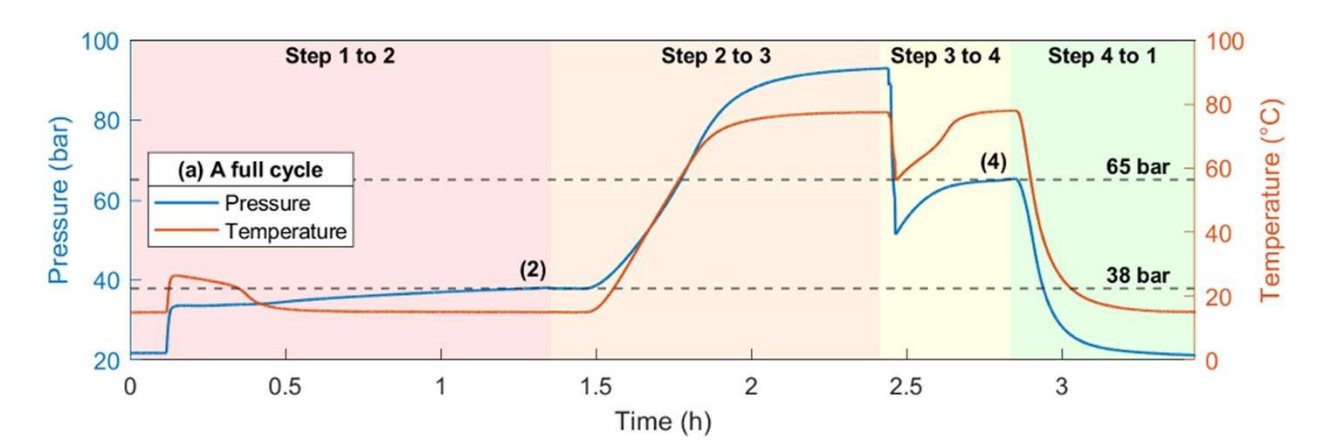


UoN alloy (Ti,Zr)CrMnFeX at 25 °C

Fast reaction kinetics based on AB2 alloys to match system response

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Integrated MH single stage compressor: Using sea water 15˚C and electrolyser 80˚C

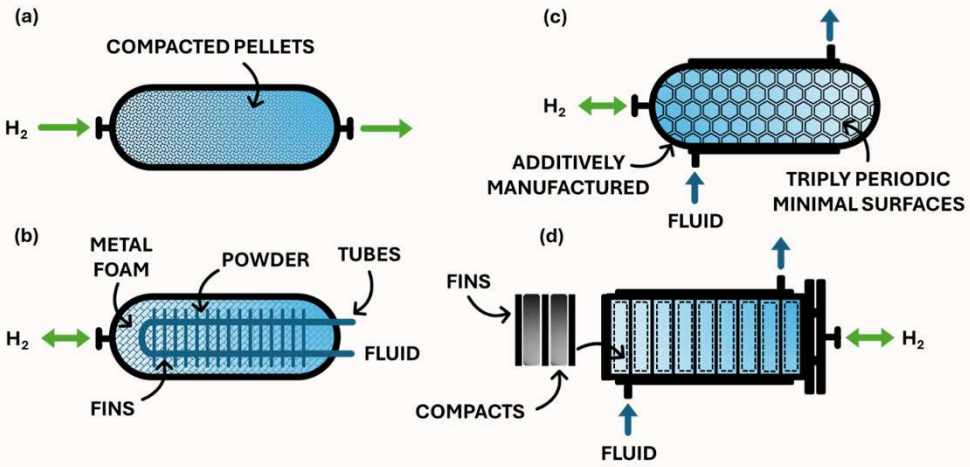




Suitability of Metal Hydride Compression at Offshore Hydrogen Generation for Use in Transmission Pipelines
Jorge Montero Banuelos, Marcus Adams, Andrew Gray, Ramas Al Qudah, Alastair Stuart, Shumao Wang, Yuanfang Wu, Martin Dornheim, David Grant.

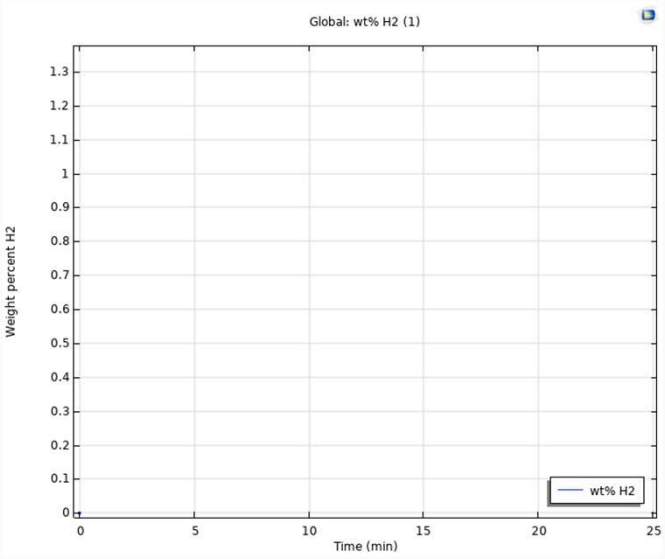
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Alternatives:

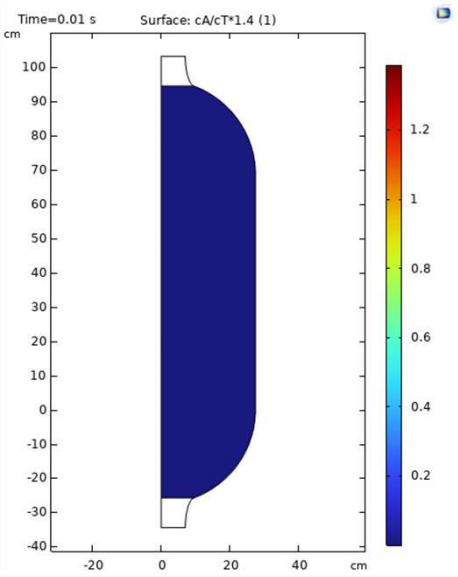


Circulating hydrogen: simulation

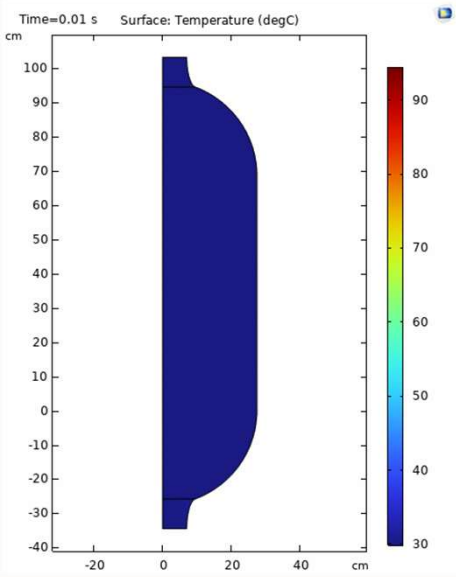
wt% H_2 profile



wt% H_2 profile

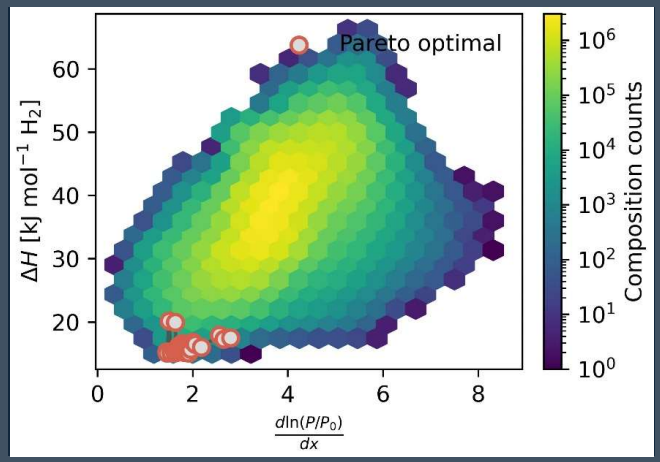


Temperature profile



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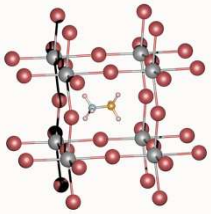
Materials selection for compressors



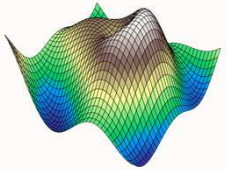
Lei Lei, David Grant, Martin Dornheim , Sanliang Ling

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Supervised machine learning in materials science



Best model $g^*(\boldsymbol{x})$ is the one gives the lowest validation loss, e.g. mean absolute error (MAE)



Materials → Representations → $g(\boldsymbol{x})$ → Target properties

Representations
- Chemical composition based
- Atomic position based

Experimental data

Computational data

Composition models

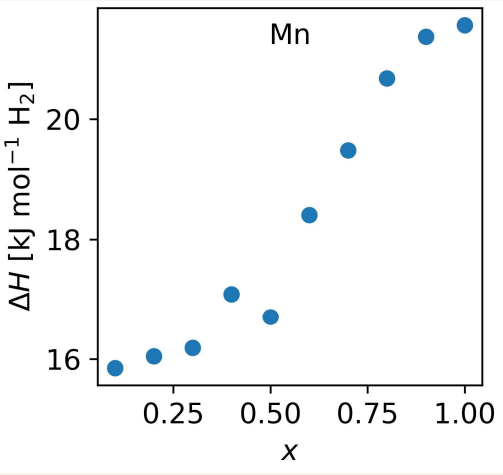
Machine learned interatomic potential

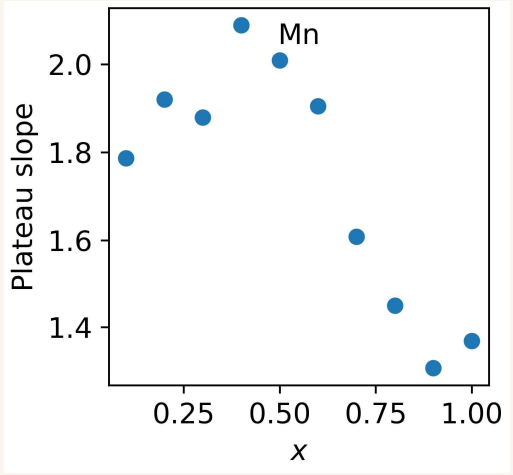
Computational and Data-Driven Modelling and Discovery of Metal Hydrides
Lei Lei, Matthew Witman, David Grant, Martin Dornheim, Sanliang Ling

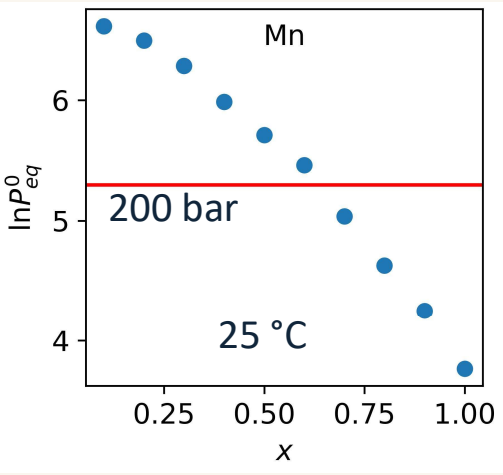
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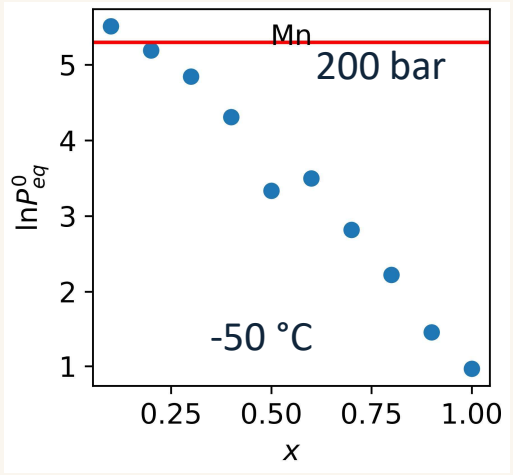
Composition design of metal alloys using machine learning

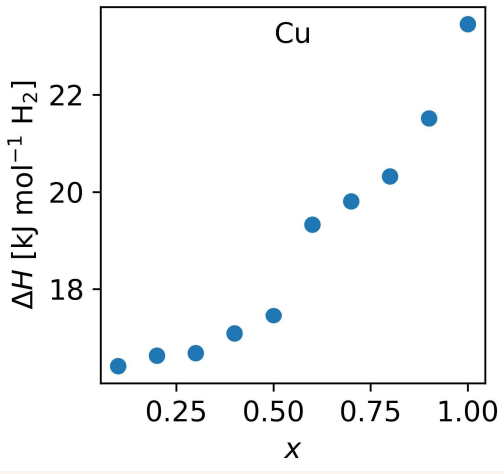
$Ti_{0.8}Zr_{0.2}Fe_{2-x}M_x$

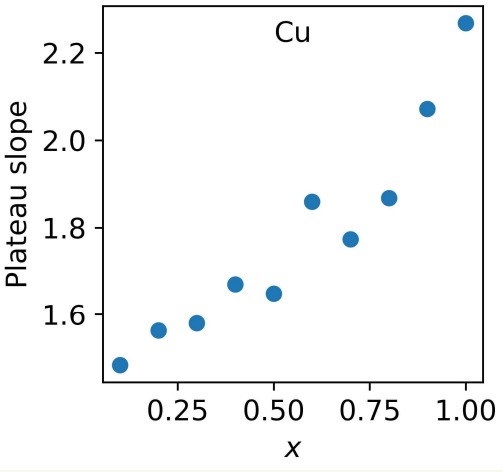


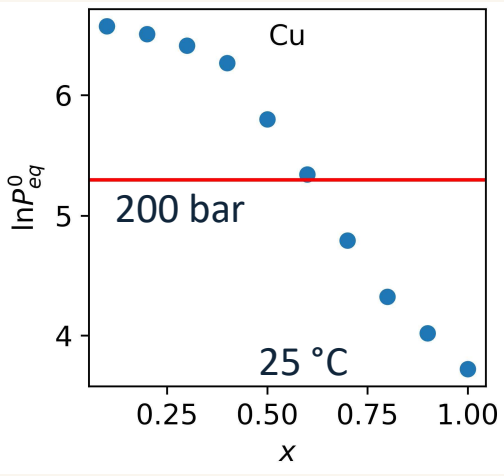


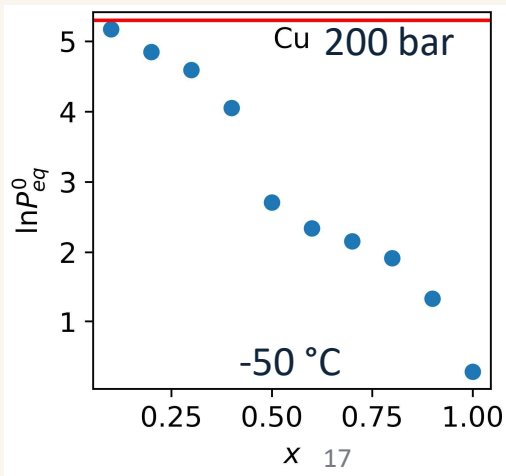






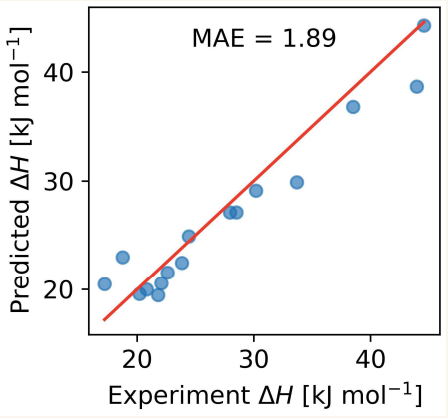




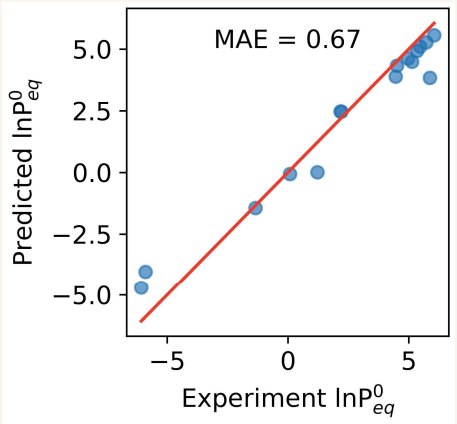


Validation of machine learning model

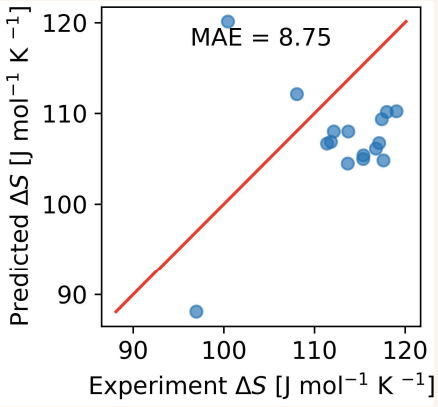
Desorption



Desorption



Desorption

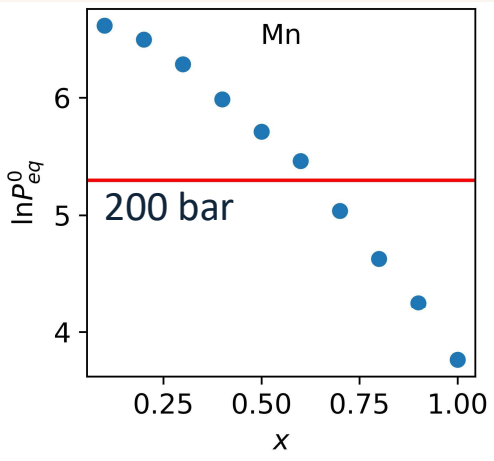


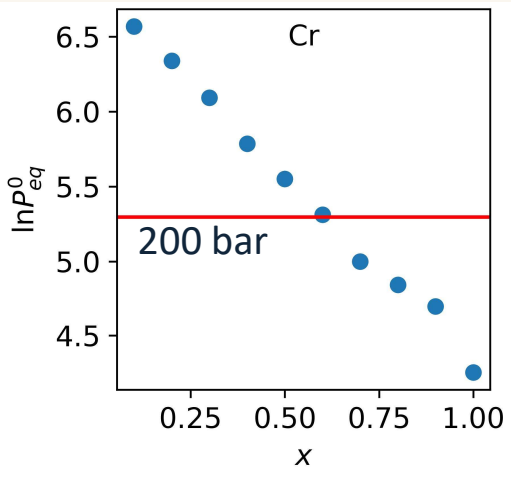
Good accuracy for ΔH

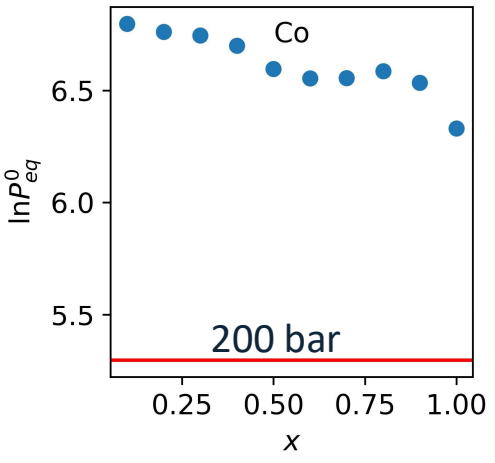
High error for ΔS due to training data noise.

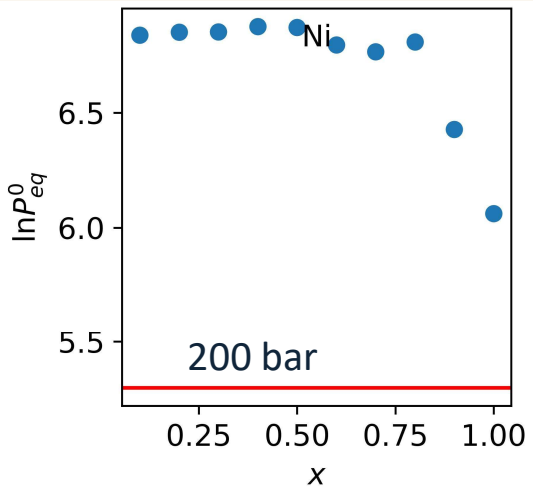
AB_2 Intermetallics

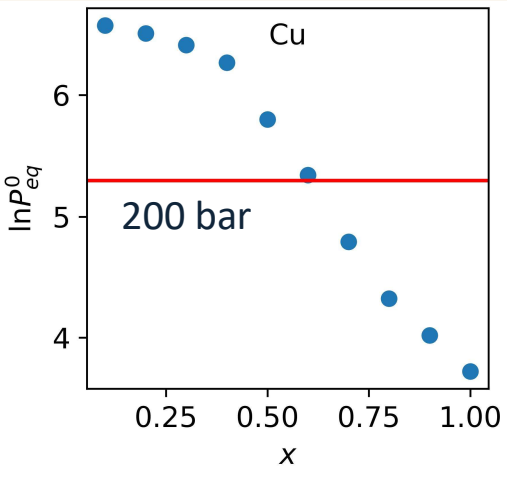
Selection based on plateau pressure



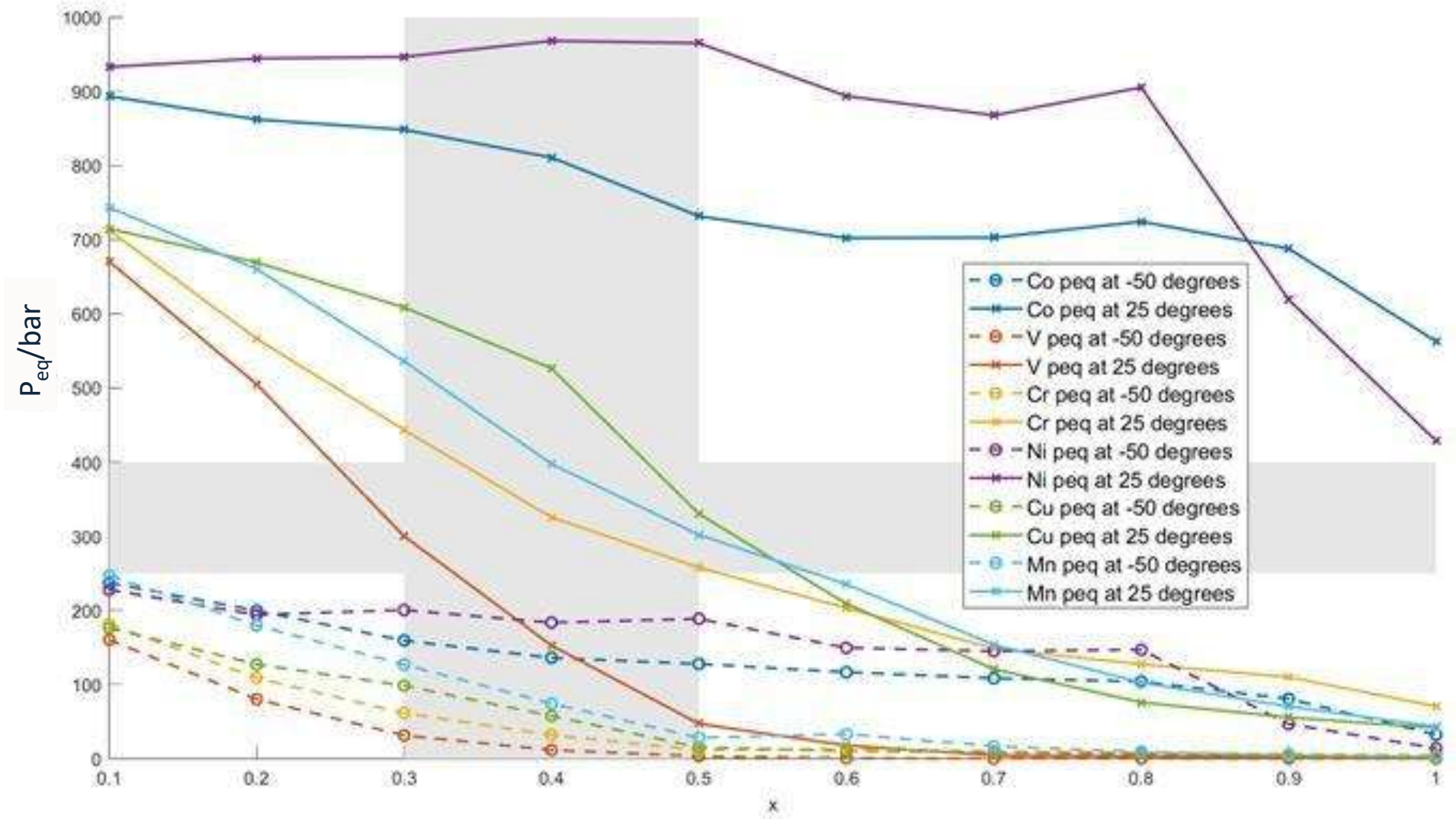


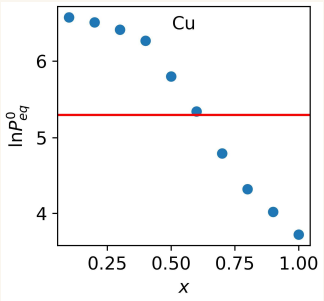


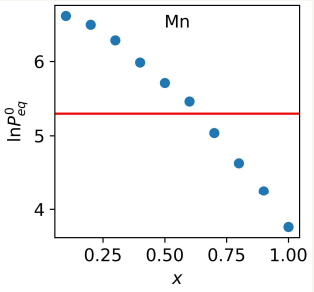


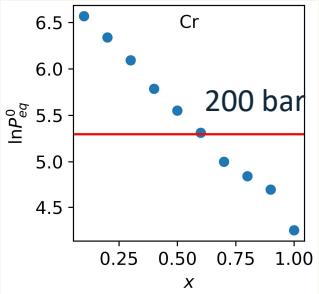


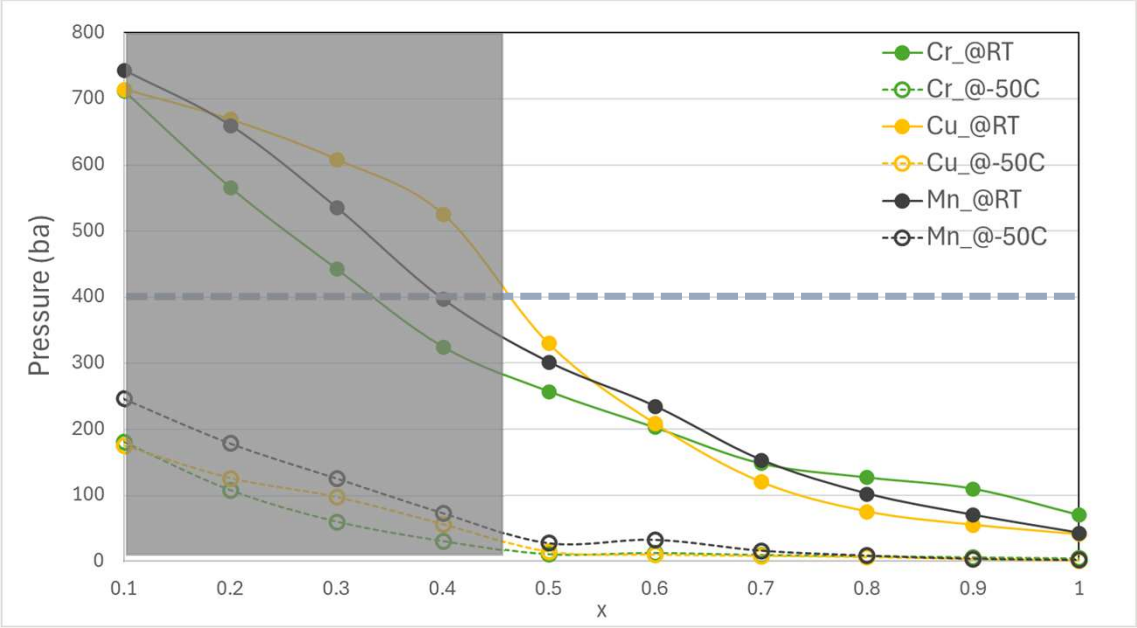
$Ti_{0.8}Zr_{0.2}Fe_{2-x}M_x$


P_{eq}/bar
x
Co peq at -50 degrees
Co peq at 25 degrees
V peq at -50 degrees
V peq at 25 degrees
Cr peq at -50 degrees
Cr peq at 25 degrees
Ni peq at -50 degrees
Ni peq at 25 degrees
Cu peq at -50 degrees
Cu peq at 25 degrees
Mn peq at -50 degrees
Mn peq at 25 degrees





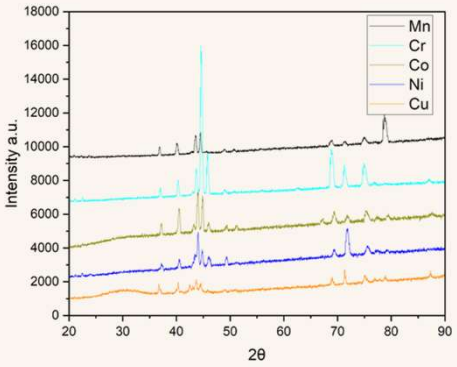




$Ti_{0.8}Zr_{0.2}Fe_{2-x}Mn_x$

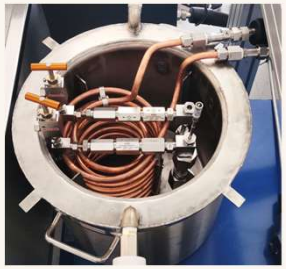
$Ti_{0.8}Zr_{0.2}Fe_{2-x}Cu_x$

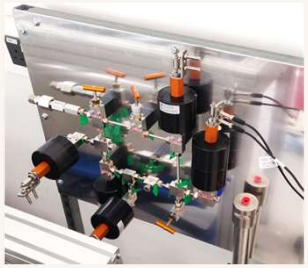
P_{eq} < 400 bar @RT
Low slope factor

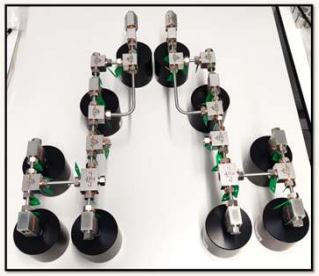


$Ti_{0.8}Zr_{0.2}Fe_{1.6}M_{0.4}$
Stirred arc melting
sample 20 -100 g
(Royce)
ICMPE Arc-melted
10-12 g

- Differential pressure measurement
- High-accuracy
- Fully automated
- Highly configurable
- Sample temperature up to 180°C
- Due for completion mid-2025







Engineering Challenges in 100 MPa Sievert's Apparatus Construction
Andrew Gray Tim Cooper, Marcus Adams, Matthew Wadge, Lei Lei, David Grant, Martin Dorheim
Investigation of Metal Alloys for High-Pressure Hydrogen Compression up to 1000 bar
Lea Gewandt, Jorge Montero Banuelos, Lei Lei, Marcus Adams, Drew Sheppard, Marek Polanski, Sanliang Ling, David Grant, Martin Dornheim

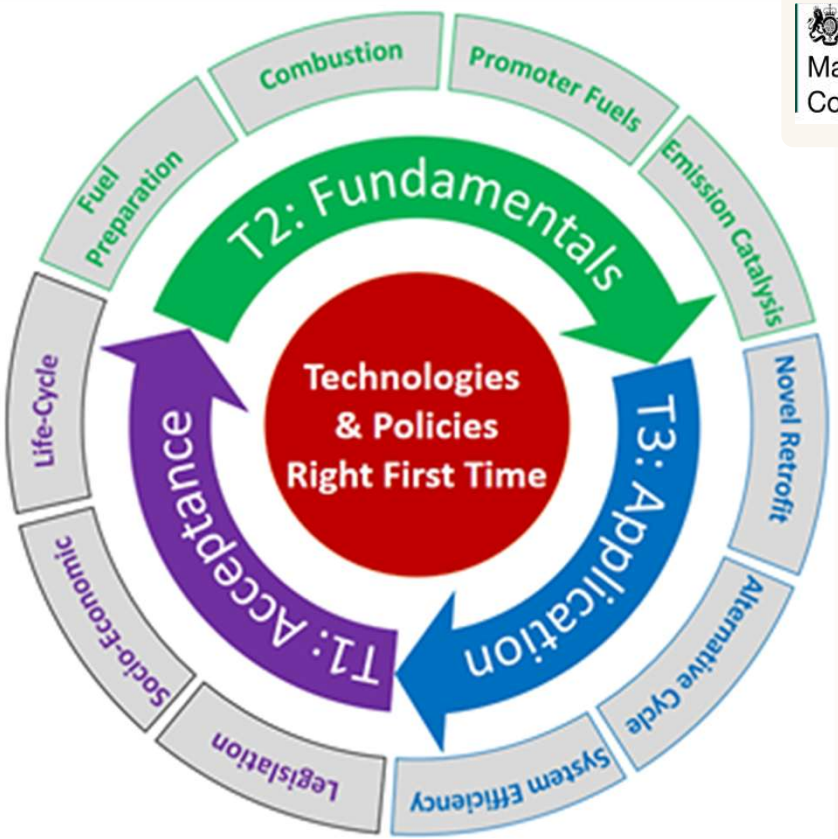
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Metal hydride - ammonia systems for onboard hydrogen fuel production

Saad Salman, Navaratnarajah Kuganathan, Sanliang Ling, David Grant



Part of the Green Ammonia Propulsion *('MariNH3')*



Maritime and Coastguard Agency

MAHLE Powertrain

Cummins

ROLLS ROYCE

DOLPHIN N2

Lloyd's Register

Infineum

Shell

Westport Fuel Systems

CORYTON advanced fuels

bp BP Shipping

Quantum ES GAS ENGINES

JM Johnson Matthey Inspiring science, enhancing life

RICARDO

BMT Group

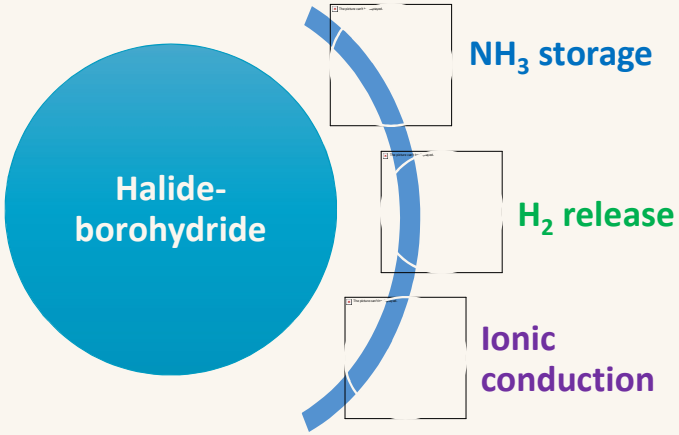
PacificGreen Technologies Group

CATAPULT Connected Places

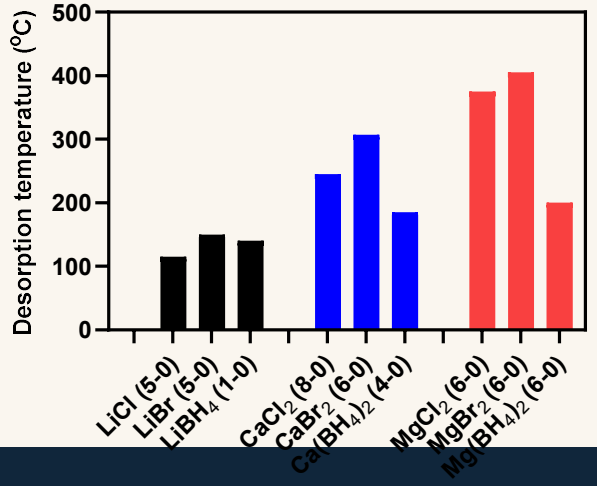
HSE Health & Safety Executive

- Nottingham led 5 year EPSRC programme grant (£5.5M funding, 2022-2027) to develop technologies and acceptance criteria around decarbonised clean marine

Halide-borohydride ammoniates



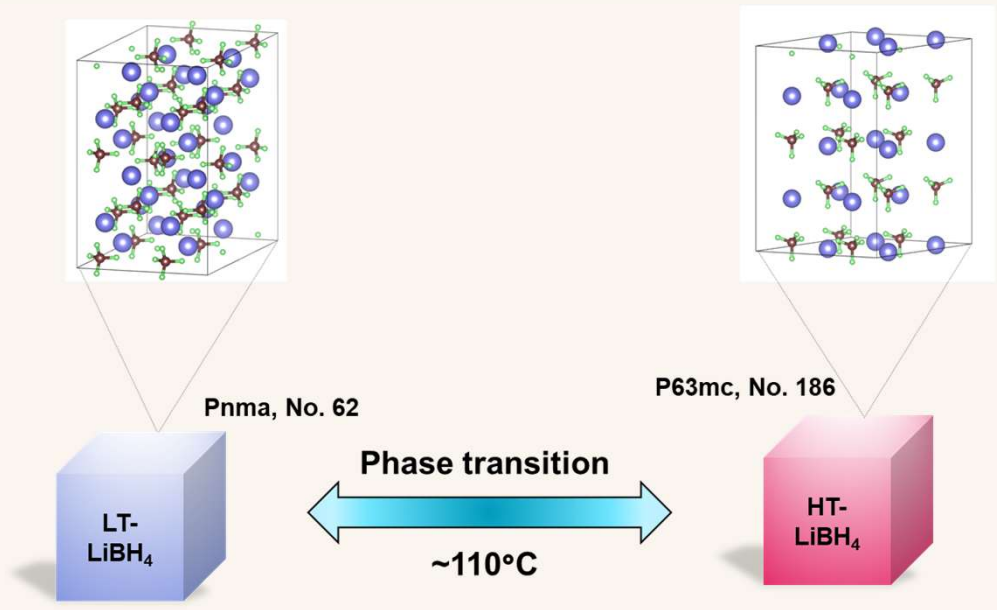
- No intermediates/byproducts or new borohydride phases
- No competing reactions e.g. Mg^{2+}-NH_3 vs Na^{+}-NH_3
- Both work as NH_3 carriers
- Halide ammoniate may keep NH_3 in vicinity of BH_4
- Enhance local NH-HB interactions

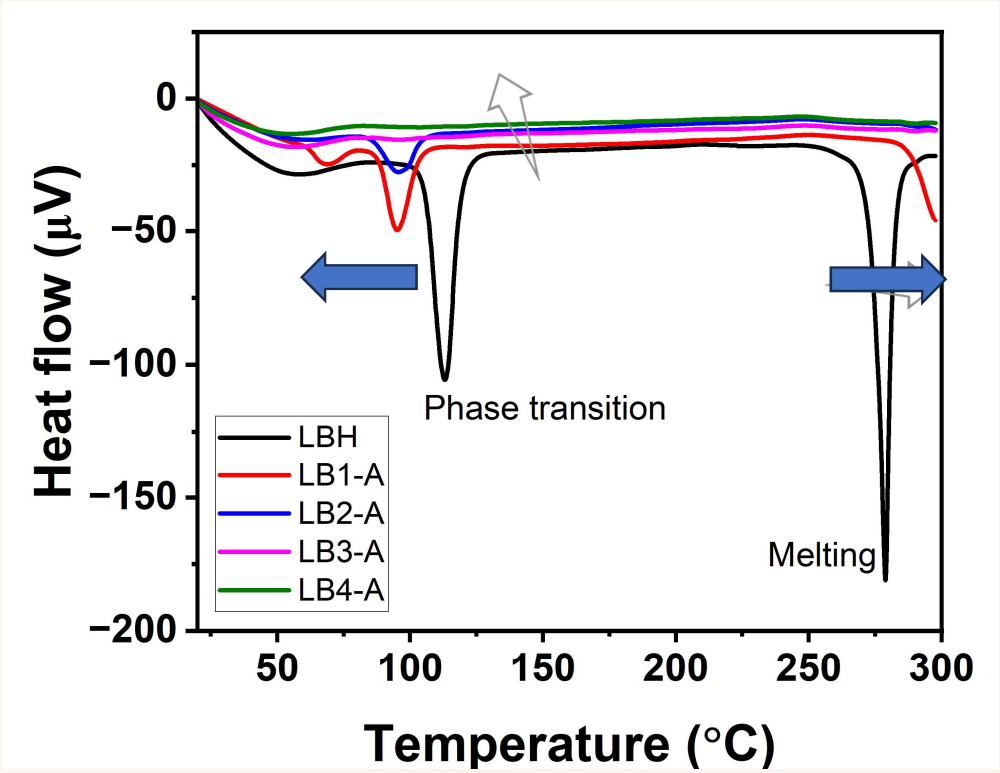




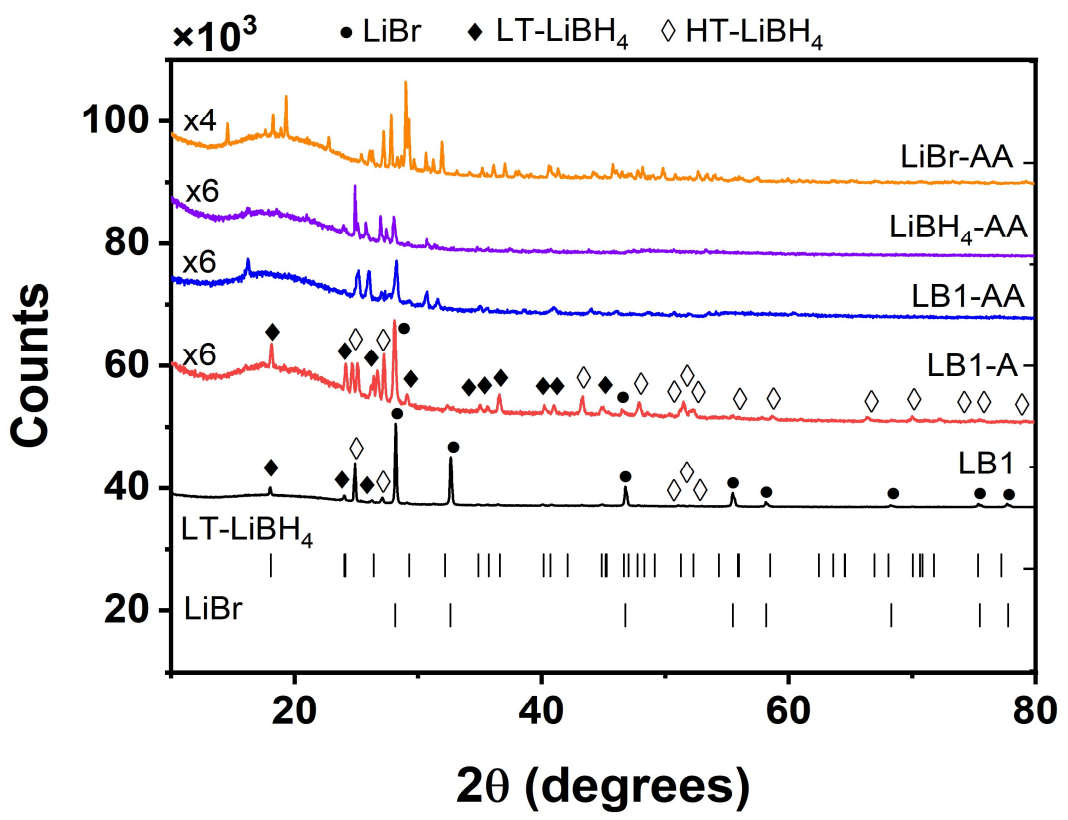
Chem. Eur. J. **2019**, 25, 6840 –6846

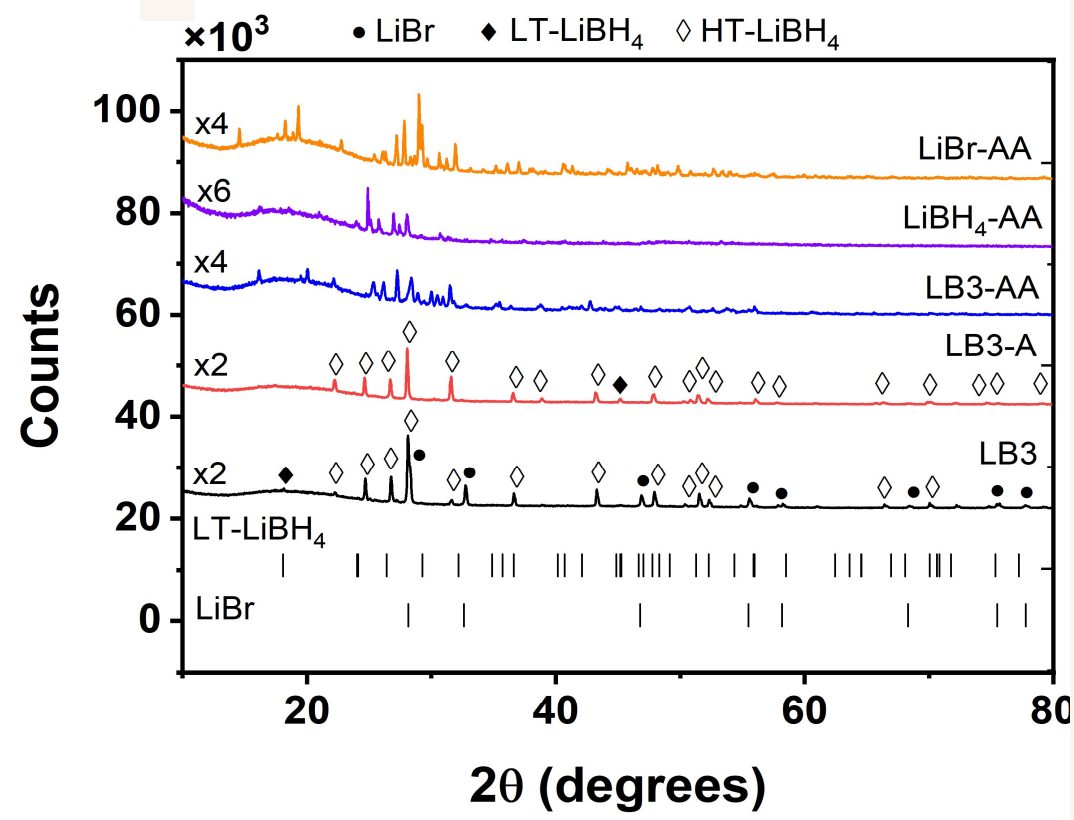
Structural and thermal analyses of $LiBH_{4-x}Br_x$ systems





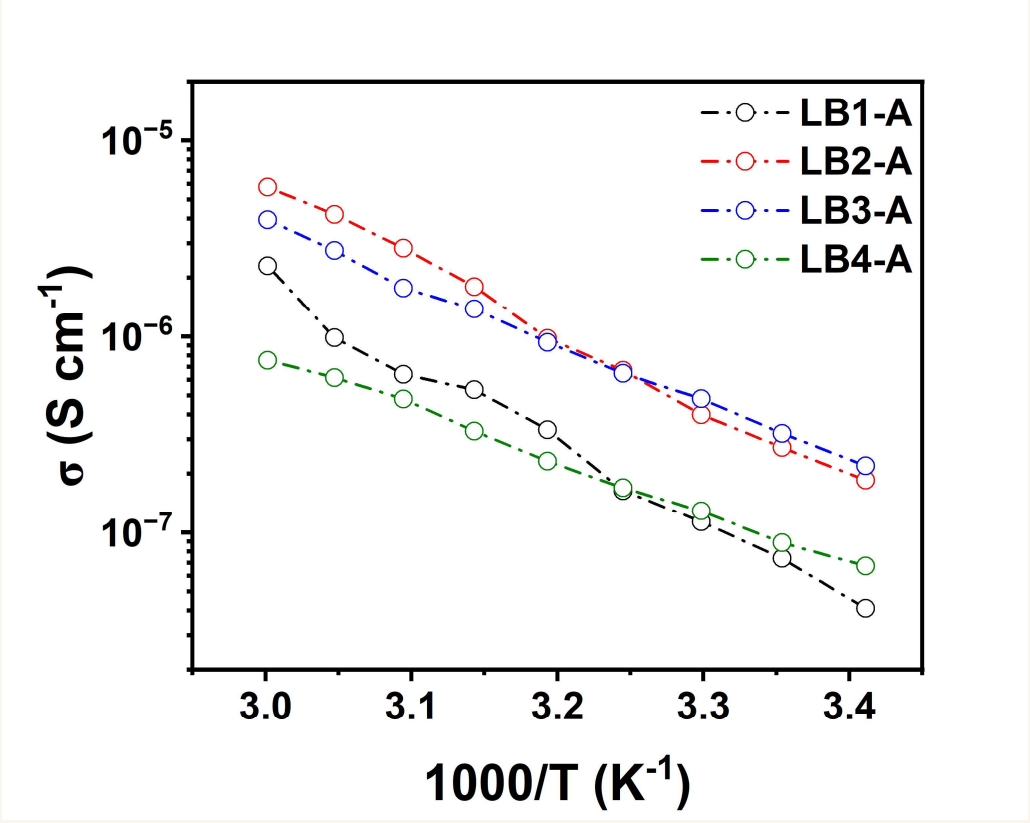
Structural analysis



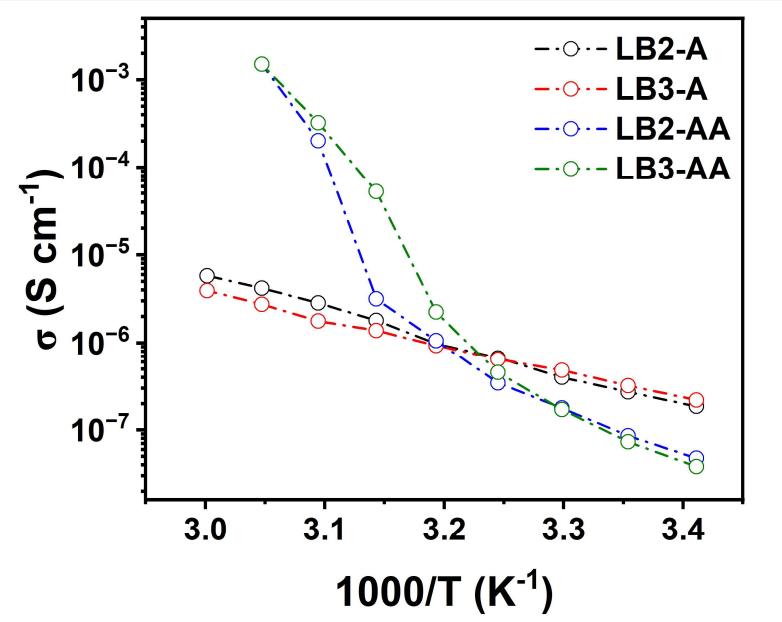


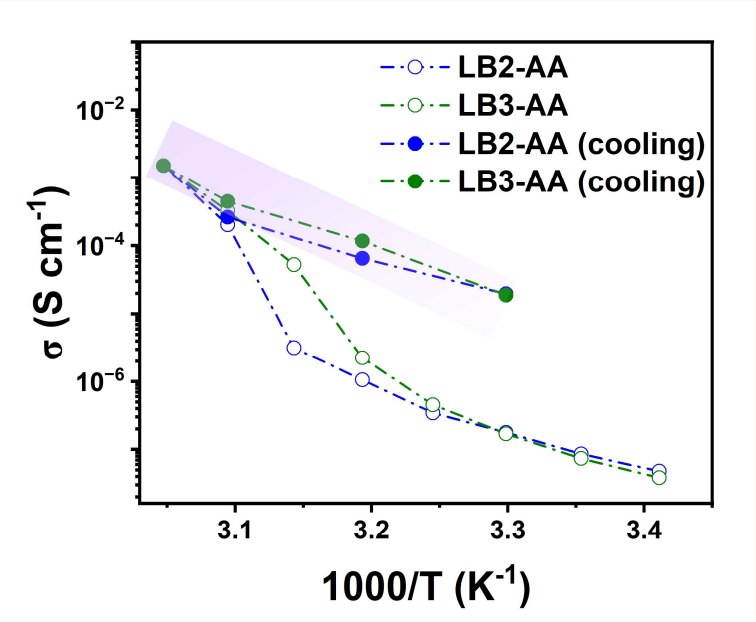
Ionic conduction – the HT $LiBH_4$ phase

The $LiBH_{4-x}Br_x$ systems

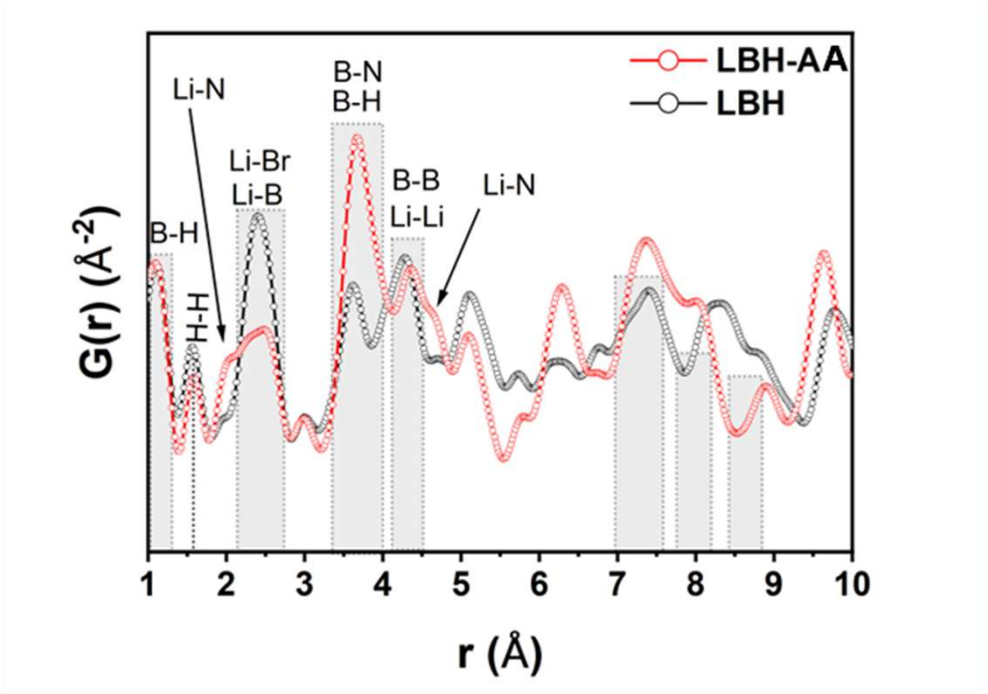


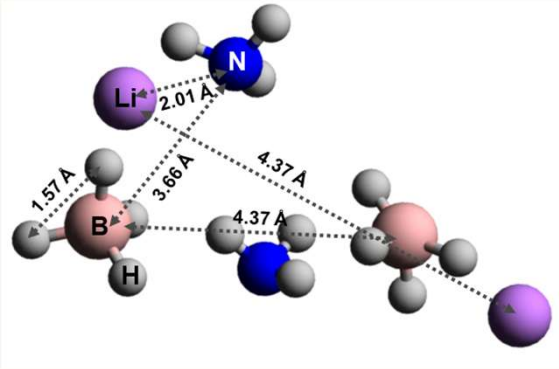
Ionic conduction – the HT $LiBH_4(NH_3)$ phase

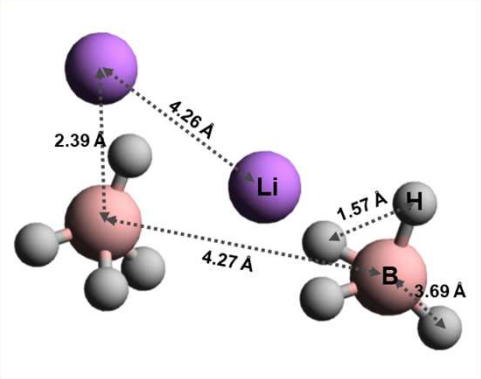




$LiBH_4$ and $LiBH_4(NH_3)$ systems

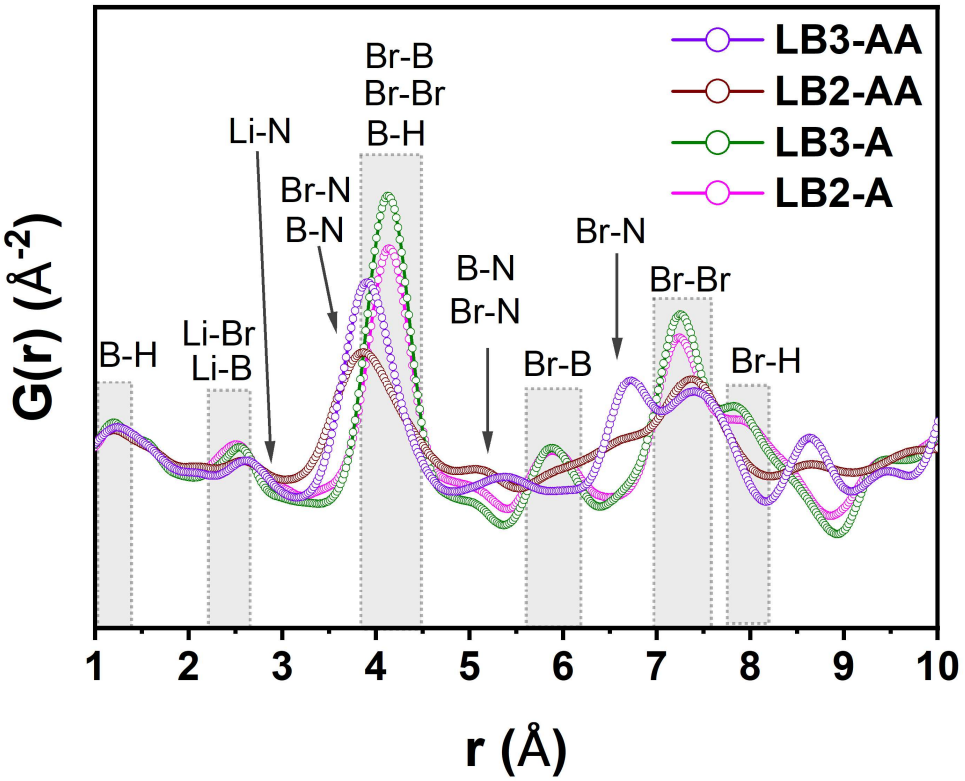






- Peak broadening in the presence of NH_3.
- Increase of distance correlates with the lattice expansion in the presence of NH_3.

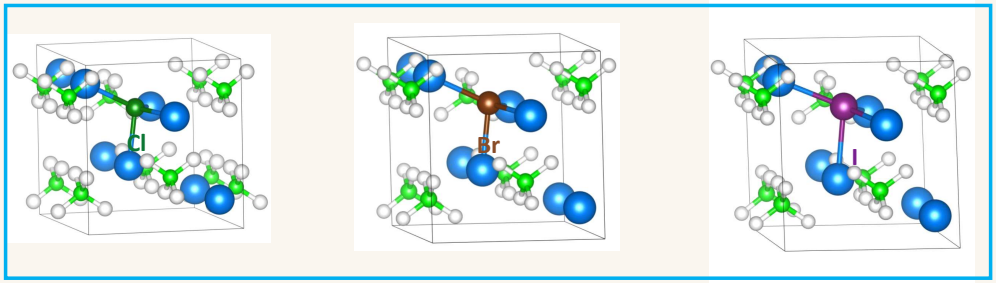
$Li(BH_4)_{1-x}$-Br_x and $Li(BH_4)_{1-x}$-$Br_x(NH_3)$ system



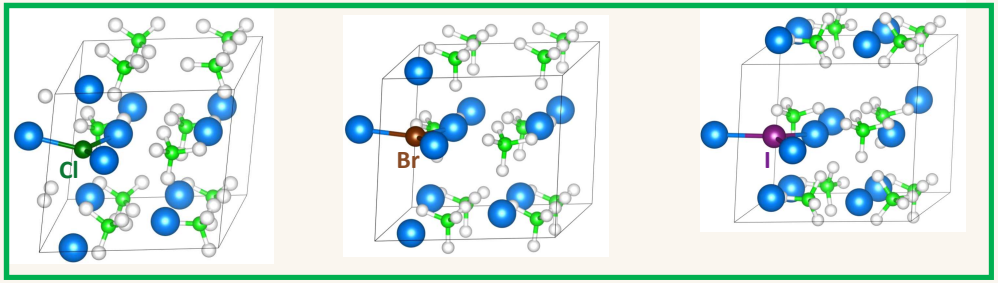
- New local pairs due to NH_3 incorporation.
- Peak shift and peak broadening suggest new bond formation (M-N) and structural disorder.

Theoretical insights from DFT

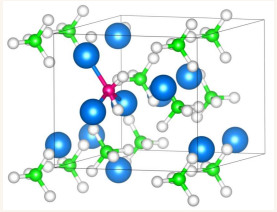
Navaratnarajah Kuganathan, Sanliang Ling



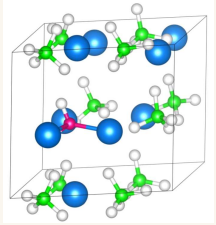
LT-$LiBH_4$ (X=Cl, Br, I)
Pnma, No. 62

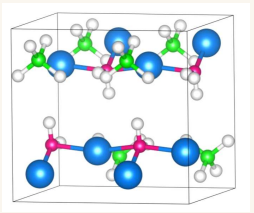


HT-$LiBH_4$ (X=Cl, Br, I)
P63mc, No. 186

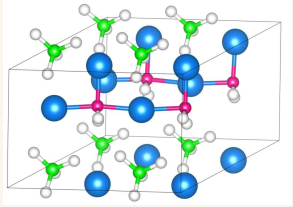


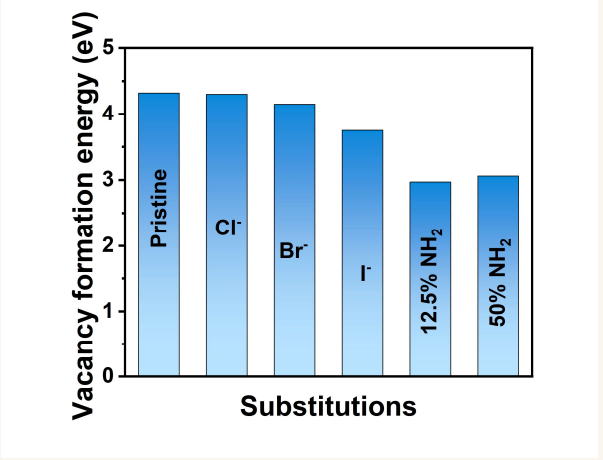
LT-$LiBH_4$ (12.5% NH_2)



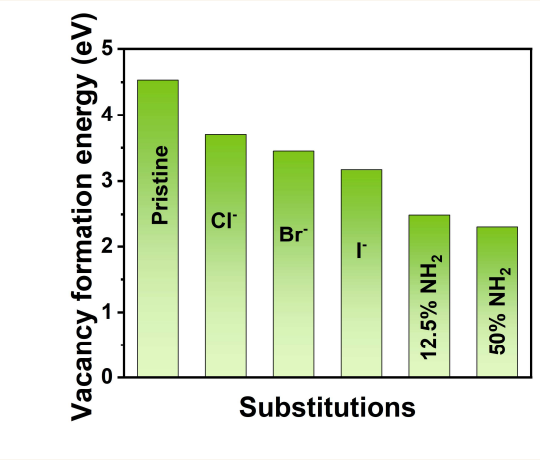


LT-$LiBH_4$ (50% NH_2)





Orthorhombic phase



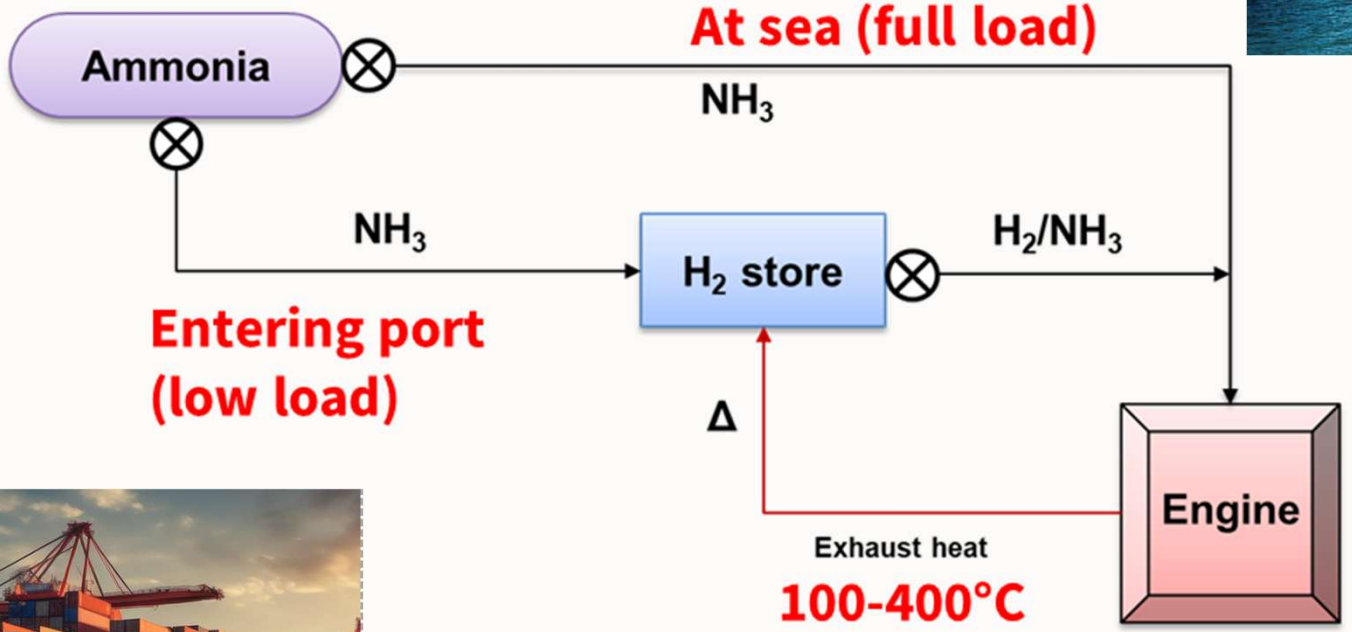
Hexagonal phase

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Practical System to reduce NO_x





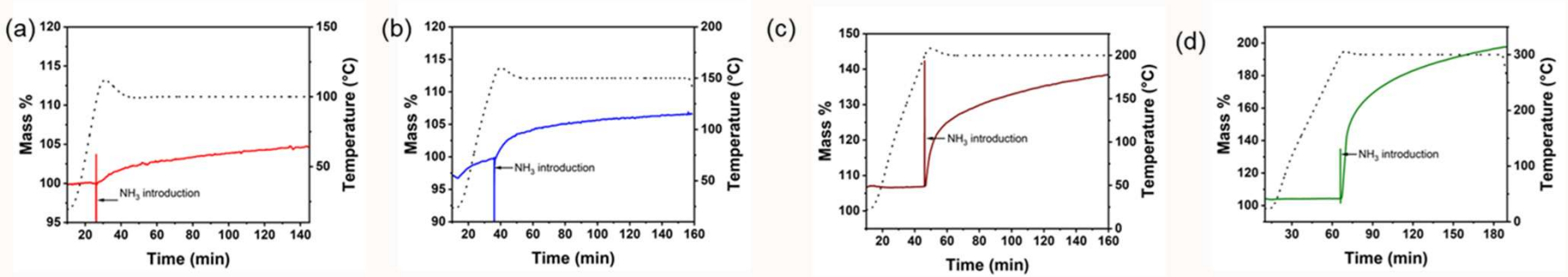


$$LiH + NH_3 \overset{\Delta}{\leftrightarrow} LiNH_2 + H_2$$

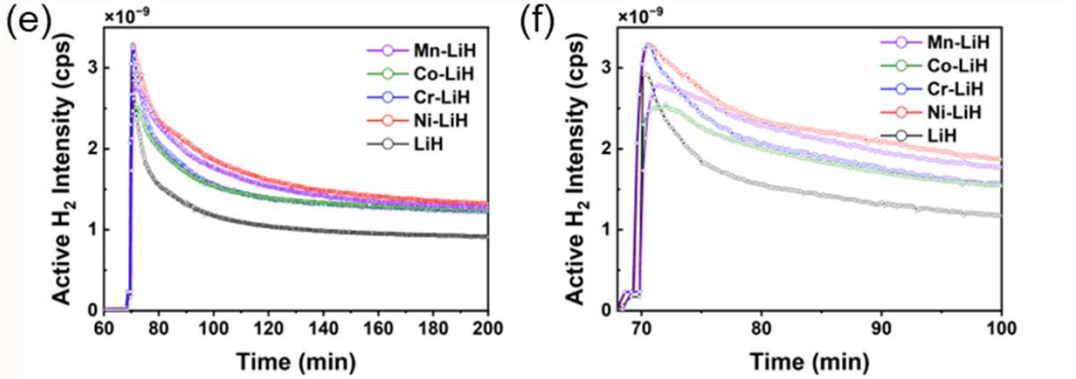
(RT, ~8.1 mass% H_2)

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Preliminary results of TM catalysts under flowing NH3

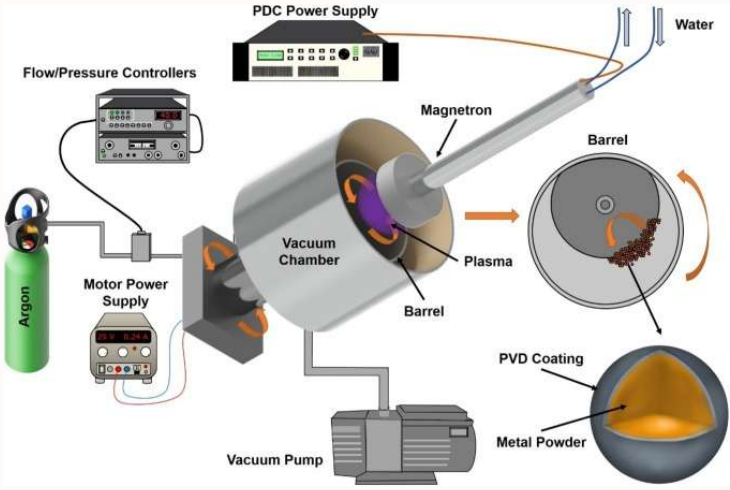


At 200 ˚C





Saad Salman, David Grant UoN
Thomas Wood, Bill David Rutherford Appleton Labs, STFC



University of Nottingham
Energy Institute

Summary

- Ammoniates can be used for several applications;
- Novel lithium-based borohydride ammoniates have been developed and are being tested as ammonia stores, and for preferential hydrogen release in the presence of catalysts;
- Lightweight metal hydrides have been identified and tested under ammonia flow to generate the required mix of hydrogen/ammonia for the engine;
- Slow hydrogen release kinetics and thermodynamic constraints are needed to be overcome; and
- Simulation models need to be developed for the ammonia-hydride system to study their reaction kinetics and predict and optimise future system-level trends.
- Hydride-nitride based systems for ammonia cracking and synthesis

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Reactive Hydride Composites

Nicholas Hall, Luke Woodliffe, Sweta Munshi, Navaratnarajah Kuganahtan, Sanliang Ling, David Grant, Martin Dornheim

University of Nottingham
Energy Institute

$Mg(NH_2)_2$–LiH–$LiBH_4$ Tri-Component Systems for Solid-State Hydrogen Storage

- The $Mg(NH_2)_2$-LiH system (Li-Mg-N-H), also known as a metal amide-hydride system, is indeed considered a promising material for hydrogen storage.
- Adding selected amounts of a borohydride ($LiBH_4$) to the Li-Mg-N-H reaction systems enhances both desorption and absorption processes and improves operating conditions.
- This potential composition 6 $Mg(NH_2)_2$ + 9 LiH + $LiBH_4$ can reversibly store and release 3.6 % wt H_2 (corresponding to 80 % of the capacity) and the inclusion of $LiBH_4$ has reduced both activation energy and reaction enthalpy.

$$\mathbf{6\ Mg(NH_2)_2\ +9\ LiH\ \rightarrow\ 3\ Li_2Mg_2(NH)_3\ +3\ LiNH_2\ +9\ H_2} \qquad \Delta H = 40.1\ kJ\ (molH_2)^{-1}$$

$$\mathbf{6\ Mg(NH_2)_2\ +\ 9\ LiH\ +\ LiBH_4 \leftrightarrow 3\ Li_2Mg_2(NH)_3\ +\ Li_4(BH_4)(NH_2)_3\ +9\ H_2} \qquad \Delta H = 35.8\ kJ\ (molH_2)^{-1}$$

- The formation of $Li_4(BH_4)(NH_2)_3$ plays a crucial role in improving the thermodynamic and kinetic behaviors of 6 $Mg(NH_2)_2$ + 9 LiH + $LiBH_4$ system.

  Thermodynamics: Exothermic reaction of $LiBH_4 + 3\ LiNH_2 \rightarrow Li_4(BH_4)(NH_2)_3$ −13.5 kJ/mol (theory)
  Kinetics: Fast Li-ion conductivity in $Li_4(BH_4)(NH_2)_3$

Our primary focus is to validate theoretically the available experimental investigation on tri-component systems and construct different reactions yielding possible desorption products with high gravimetric densities of hydrogen and low hydrogen desorption enthalpies.

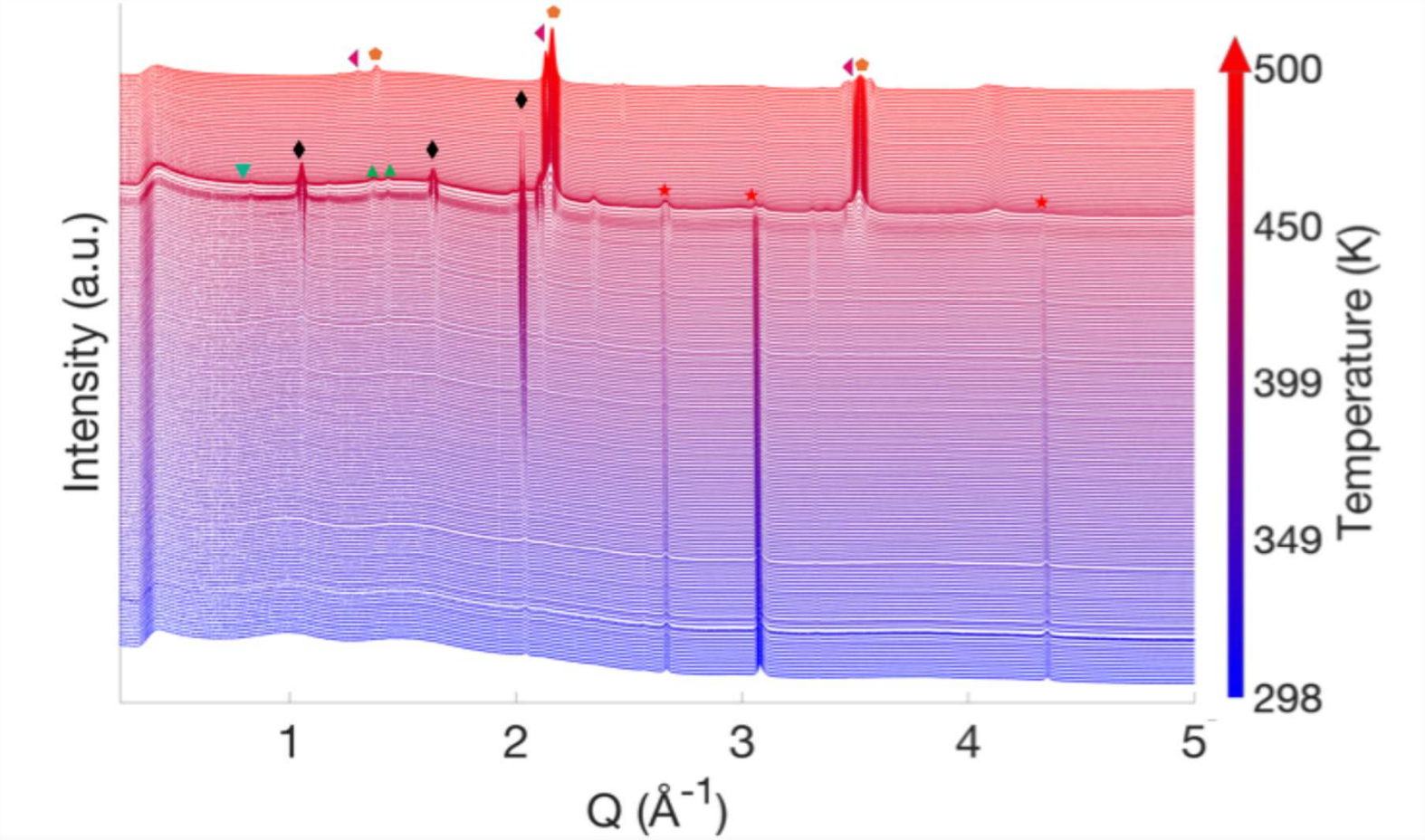
$$\mathbf{x^*Mg(NH_2)_2\ +\ y^*LiaH\ +\ z^*LiBH_4 \leftrightarrow a^*Li\text{-}Mg\text{-}N\text{-}H\ +\ b^*Li\text{-}B\text{-}N\text{-}H\ +\ c^*H_2}$$

25 and 30 kJ/mol·H_2: suitable for solid-state hydrogen storage applications at ambient conditions.

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In-situ SR-PXRD of the 6:9:1 system

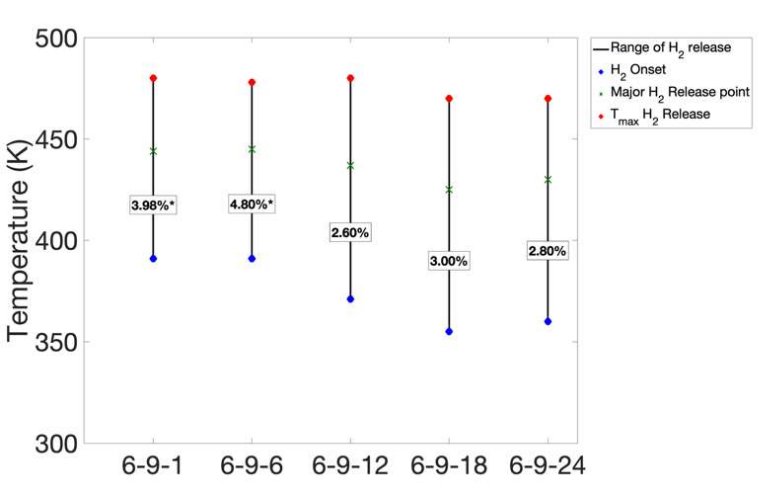
$$6Mg(NH_2)_2 + 9LiH + LiBH_4 \rightleftharpoons Li_4(BH_4)(NH_2)_3 + 3Li_2Mg_2(NH)_3 + 6H_2$$

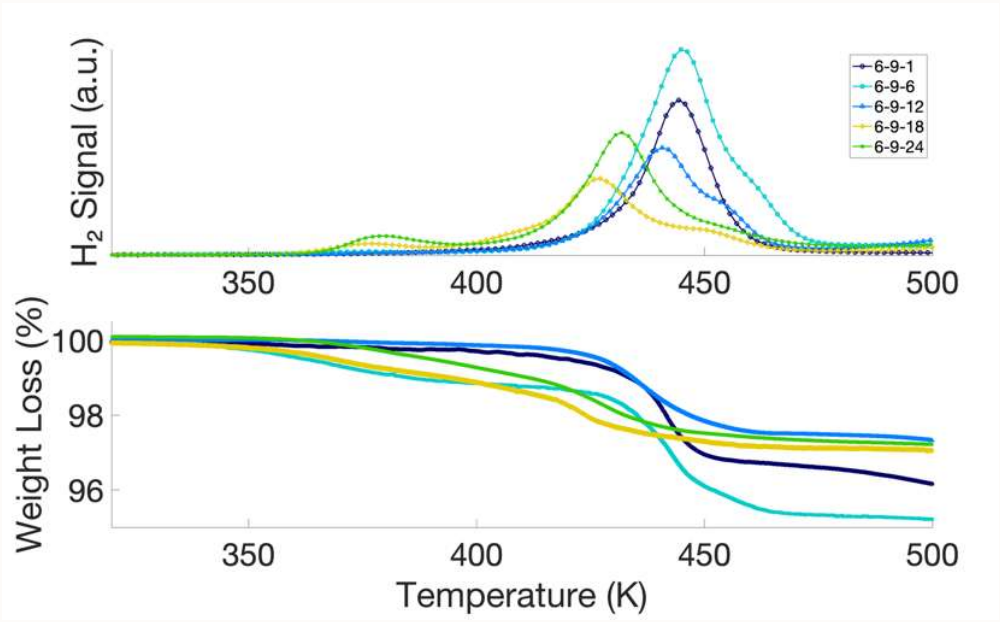


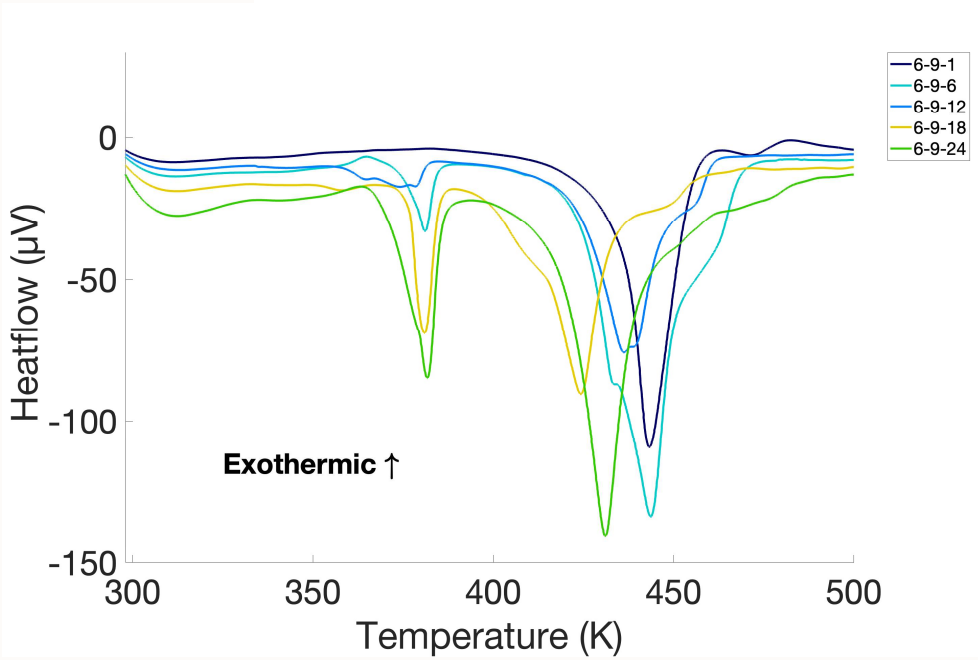
- $Mg(NH_2)_2$
- Oct - $LiBH_4$
- LiH
- Hex - $LiBH_4$
- MgNH
- $Li_4(BH_4)(NH_2)_3$
- $Li_2Mg_2(NH)_3$

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Effect of ratios







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Rail application: Vanguard

Marcus Adams, Alastair Stuart, Jorge Montero Banuelos, Martin Dornheim, David Grant

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Diesel shunter conversion to hydrogen

Class 08 diesel shunter in preparation for its conversion to hydrogen power by Vanguard Sustainable Transport Solutions



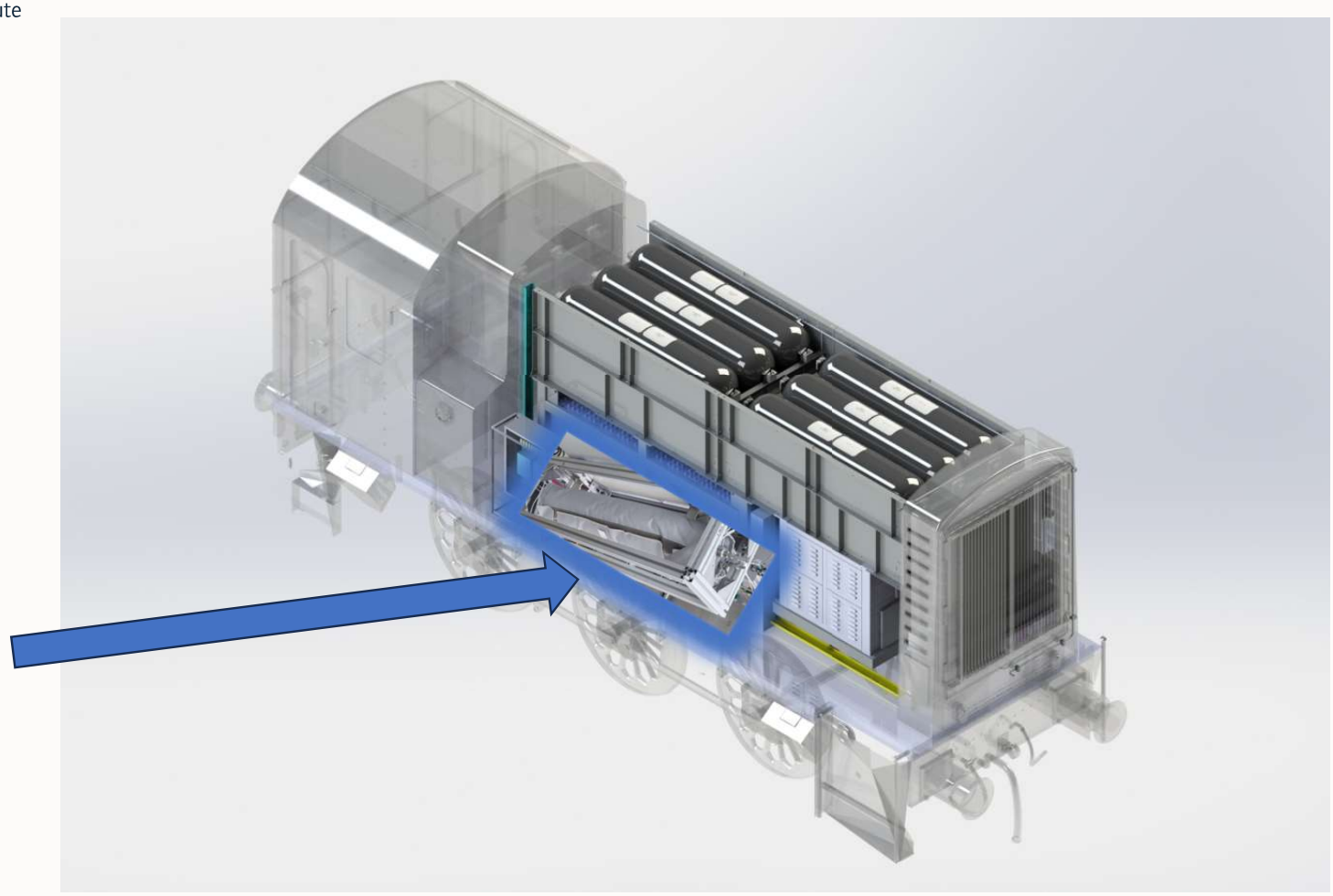
Metal Hydride tank targets:

- bespoke tank with internal architecture for heat management.
- metal hydride containing approximately 0.25 kg of hydrogen.
- Tank test tank at 0.020 - 0.055 g/s or 15 - 40 NL/min. That is 10% of the expected flow rate of the HydroShunter
- Remainder to be provided by compressed gas

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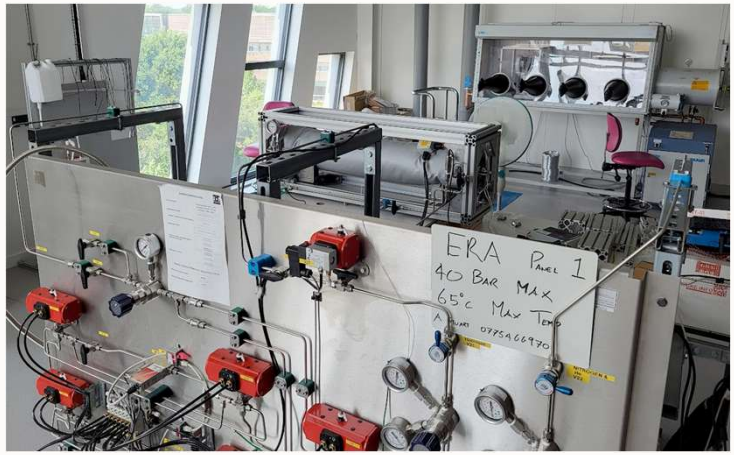
Diesel shunter conversion to hydrogen

MH Tank Location

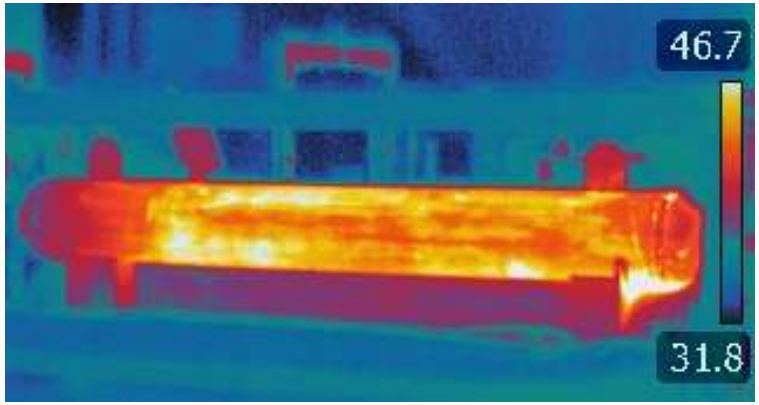


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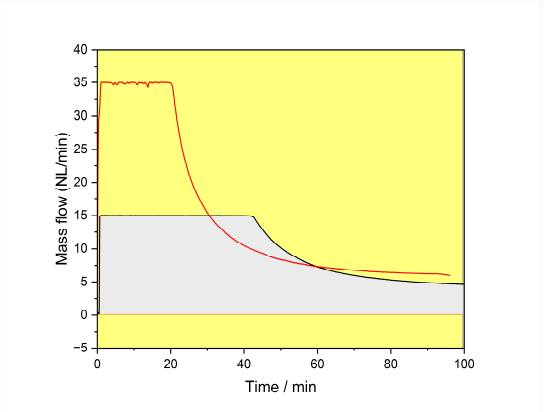


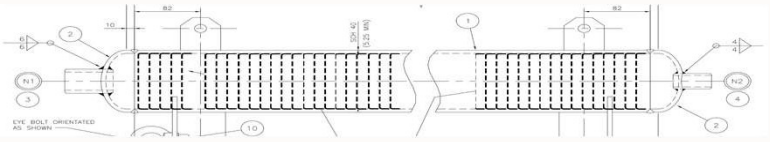


Tank is on test 20 kg of AB_2 ($Ti_{0.95}$ $Zr_{0.05}Mn_{1.46}V_{0.45}Fe_{0.09}$)









Water cooling tank/electric jacket

University of Nottingham
Energy Institute

Cooling

Elizabeth Aggathanggelo, Jorge Montero Banuelos, Marcus Adams, Lei Lei, Martin Dornheim, Alastair Stuart, David Grant, Sanliang Ling

Project Background

- UK is committed to reducing carbon emissions to net zero by 2050
- The UK food chain is responsible for **18%** of the total UK energy use or 115 $MtCO_2$ emissions
- **1 million** transport refrigeration units currently operate in the EU
- Up to **24%** of the power output of a 38t refrigerated truck is required to meet refrigeration demand

Can hydrogen-based energy infrastructure facilitate the replacement of fossil fuels by sustainable energy sources in UK food cold chain?

The H2COOL Project

Project Vision: To enable the decarbonisation of the UK food cold chain through the deployment of a new **dual-use** metal hydride store

service power needs (fuel cell or internal combustion engine)



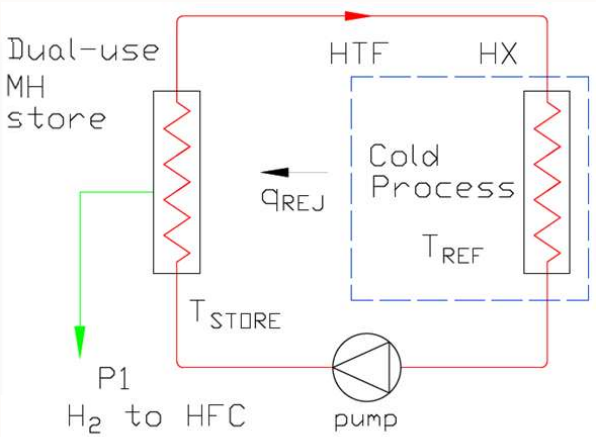
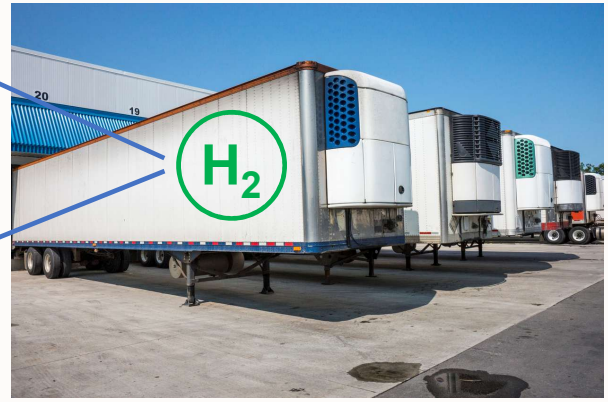


Figure 1: Schematic of the dual-use metal-hydride store

$MH + Heat \rightarrow M + \frac{1}{2}H_2$

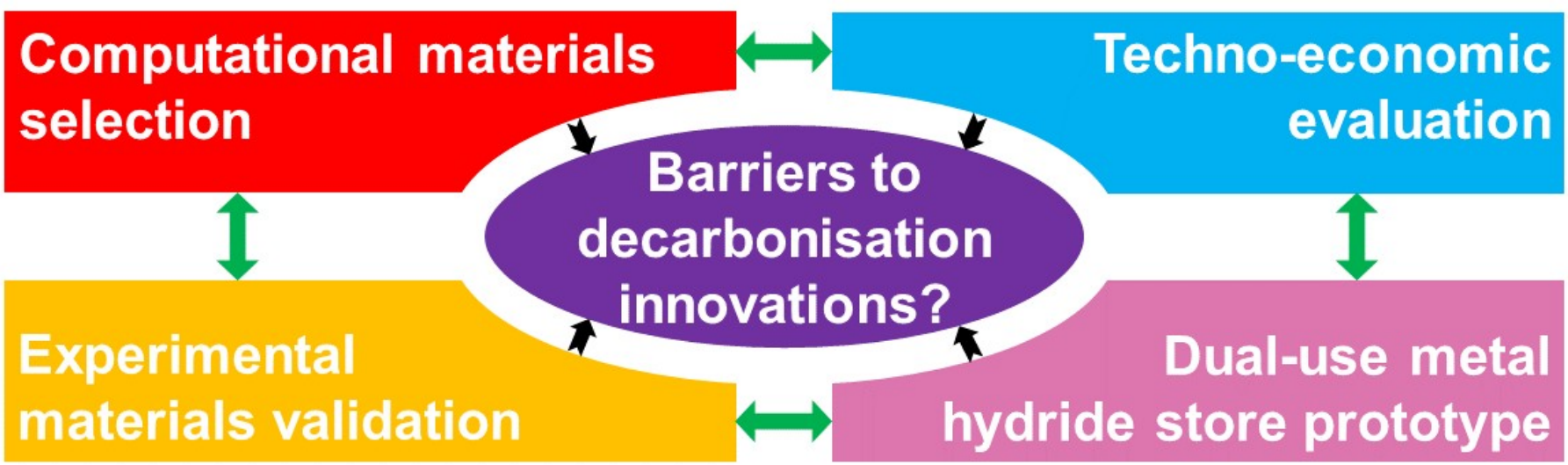
(endothermic reaction)

MH: metal hydride
M: metal (alloy)



provide direct cooling

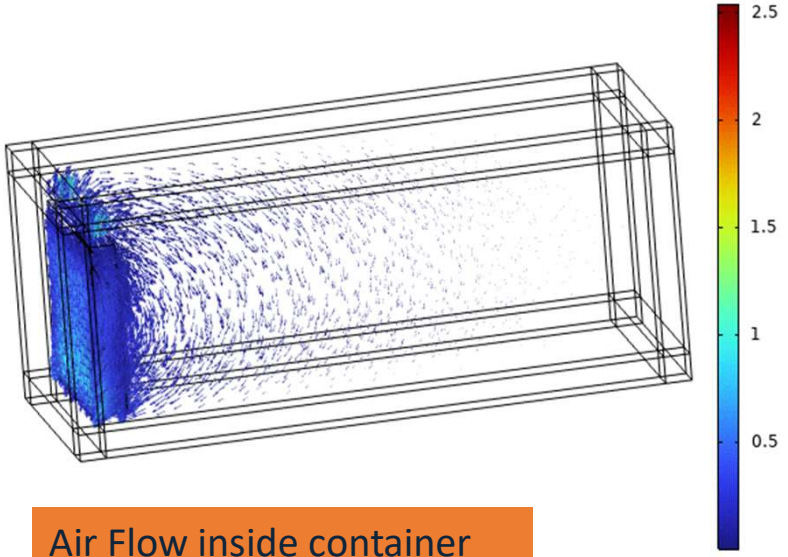
The H2COOL Project - Objectives



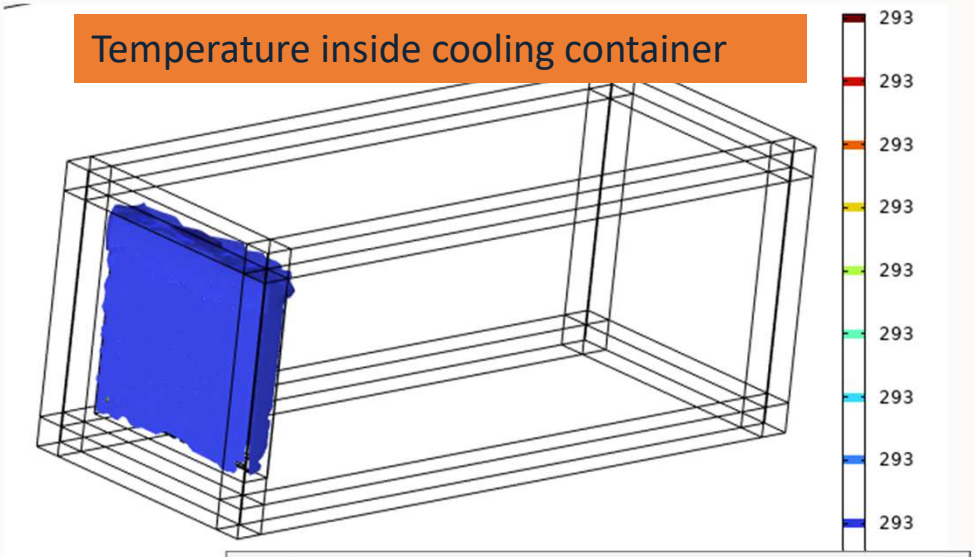
1. Computational screening to identify suitable intermetallic alloys
2. Experimental validation of the materials identified
3. User-centred study of barriers to innovation through hydrogen technology
4. Dual-use metal hydride store benchtop prototype
5. Techno-economic evaluation

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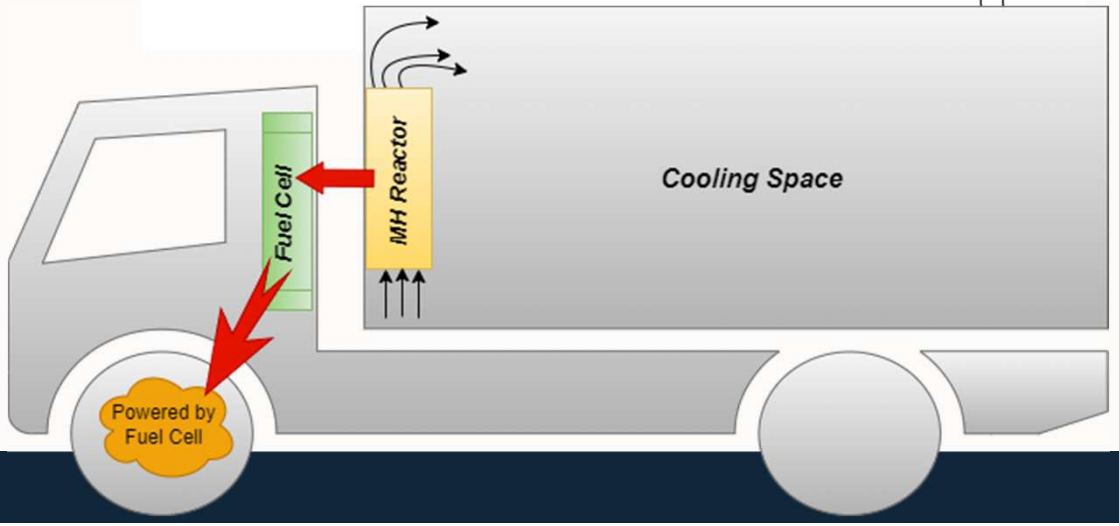
Saurabh Tiwari



Air Flow inside container



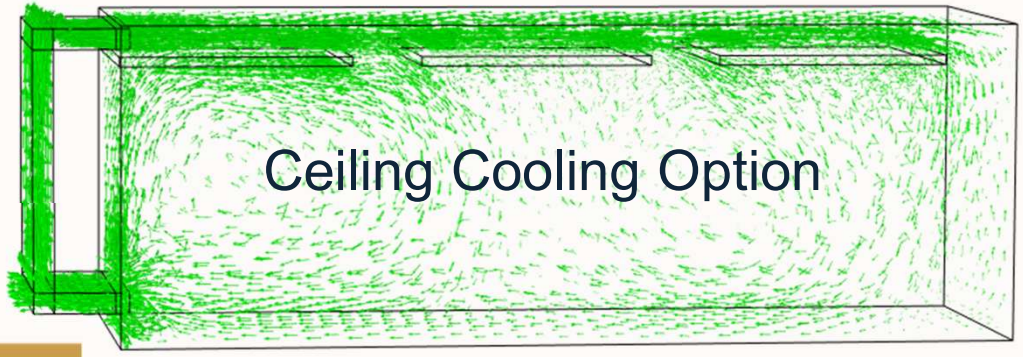
Temperature inside cooling container

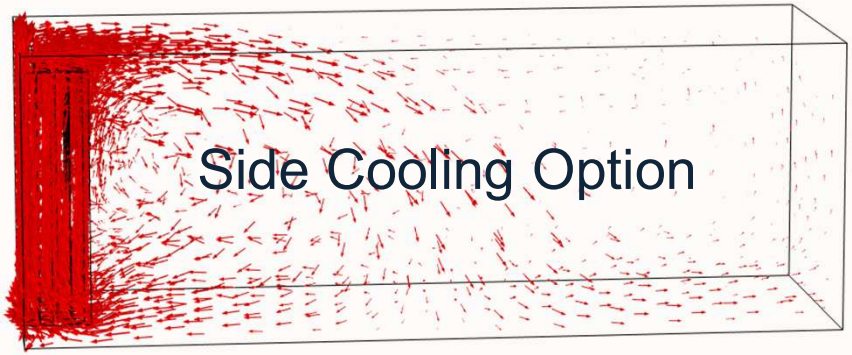


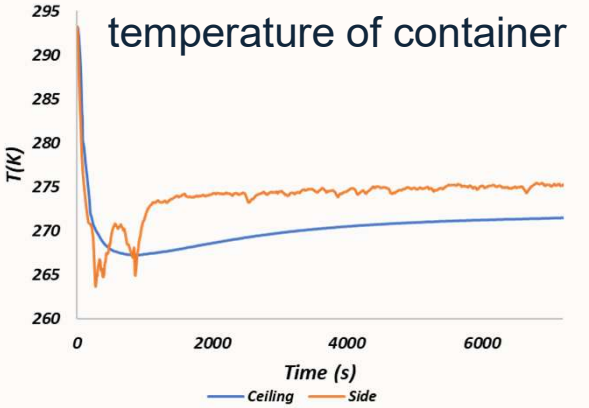
- Endothermic nature of hydrogen desorption reaction is used to cool the space
- Metal hydride reactor is integrated with fuel cell
- Anaverage temperature of as low as 260 K is achieved
- The opening of the doors modelled The speed of vehicle influences the temperature of air inside

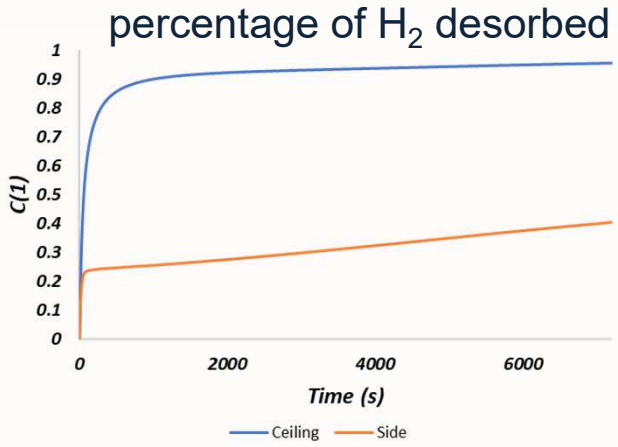
Chilled foods at 4 ˚C: Where to put the dual-use metal hydride store?





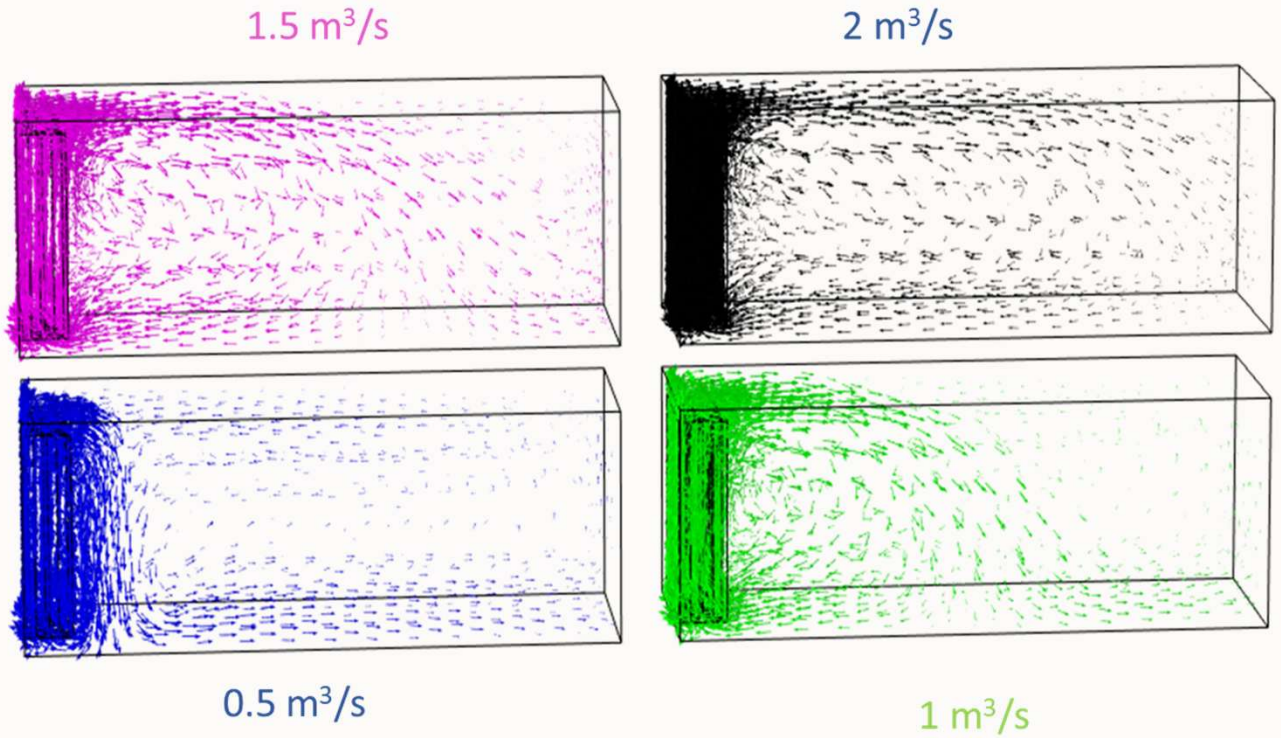


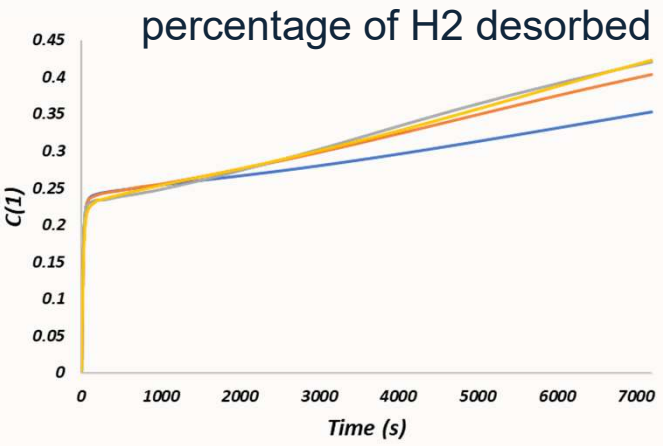


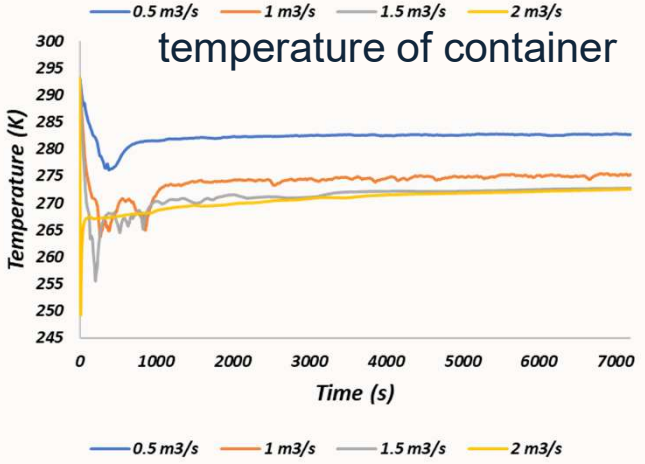


Numerical Modelling targeting 4 ˚C chilled truck

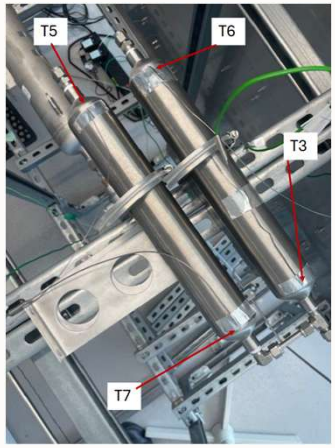
Effect of Fan Flow Rate



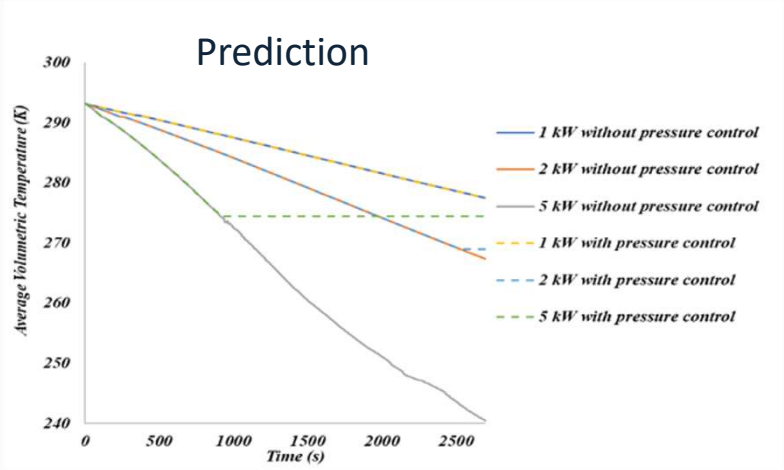


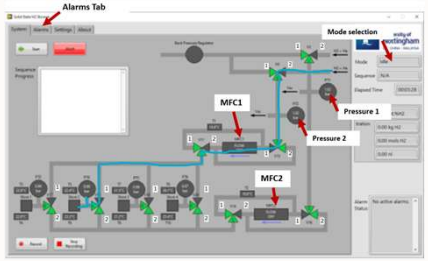


Two cylinder test: 1/8th scale

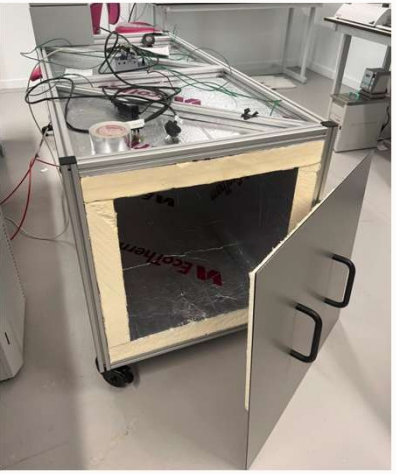




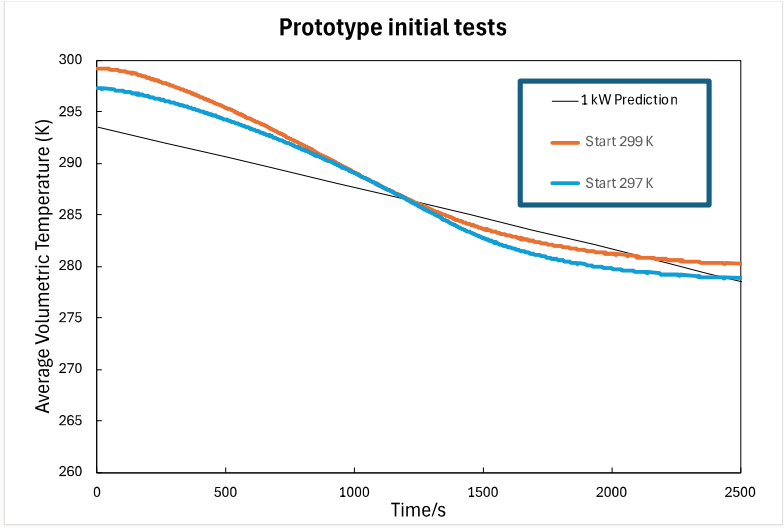








Moving onto ¼ scale

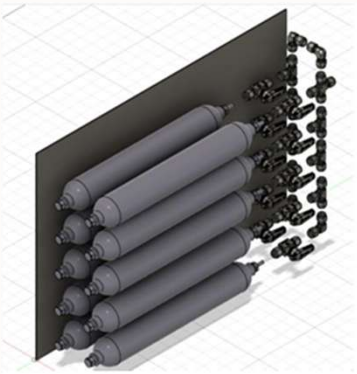


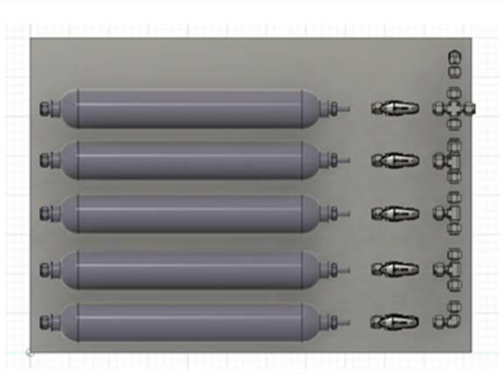
2.5 NL/min H_2

Numerical Modelling and Construction of Dual-Use Metal Hydride Store Benchtop Prototype

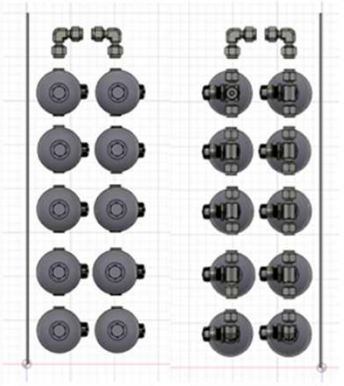
Scale Down Factor	Length (m)	Width (m)	Height (m)	Door Opening	Door Opening Time (min)	Operating Time (h)	Total Load (MJ)	MH Required (kg)
Original	6.5	2.3	2.3	2	3	2	56.31	266.7
1/2	3.25	1.15	1.15	2	3	2	11.9	55.9
1/4	1.63	0.58	0.58	2	3	2	9.1	11.3
1/6	1.08	0.38	0.38	2	3	2	0.91	4.3
1/8	0.81	0.29	0.29	2	3	2	0.5	2.4
1/16	0.41	0.14	0.14	2	3	2	0.1	0.46

MH Cylinder arrangement to deliver -20 ˚C





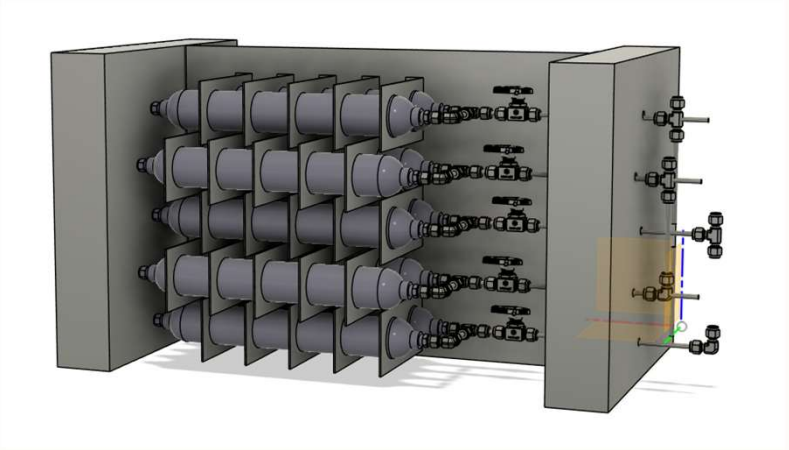
Front view

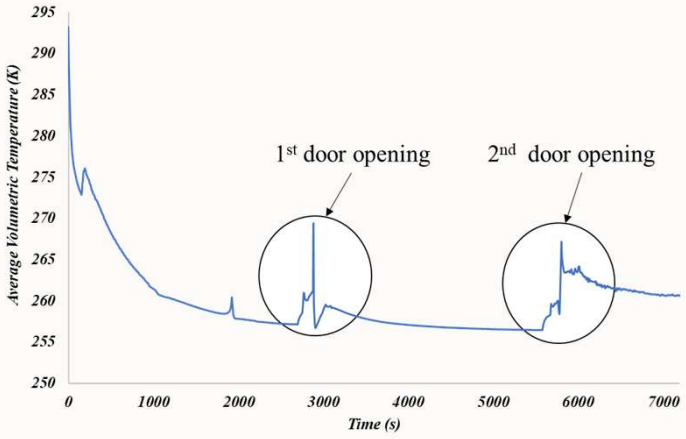


Left view

Right view

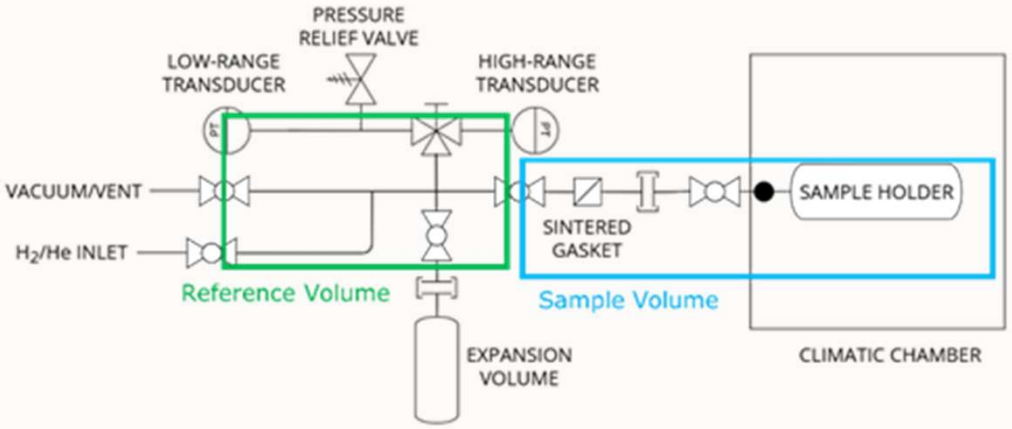
Parameter	Unit	Value
Cylinder OD	[mm]	50.8
Total cylinder length	[mm]	351
Cylinder wall thickness	[mm]	2.4
Number of cylinders	-	10
Hydralloy capacity per cylinder	[kg]	1.40
Cylinder surface area	[mm2]	52,695
Total Hydralloy capacity	[kg]	14.0
Total surface area	[mm2]	526,950

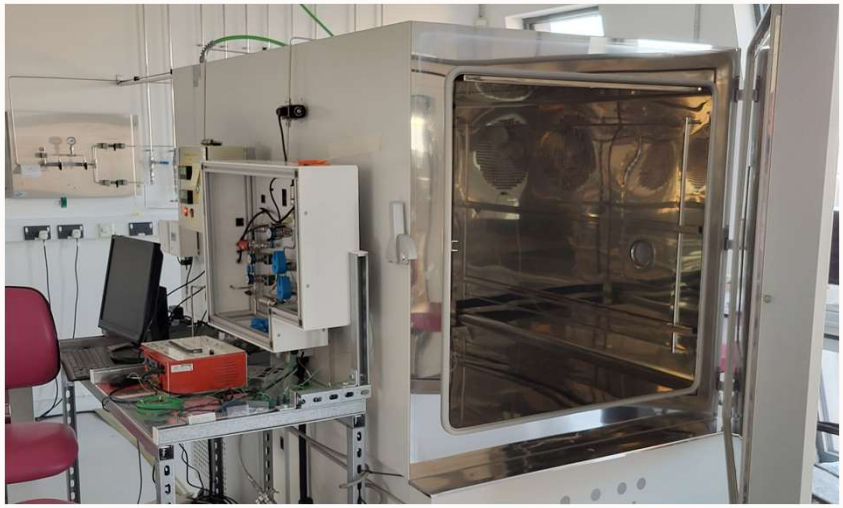




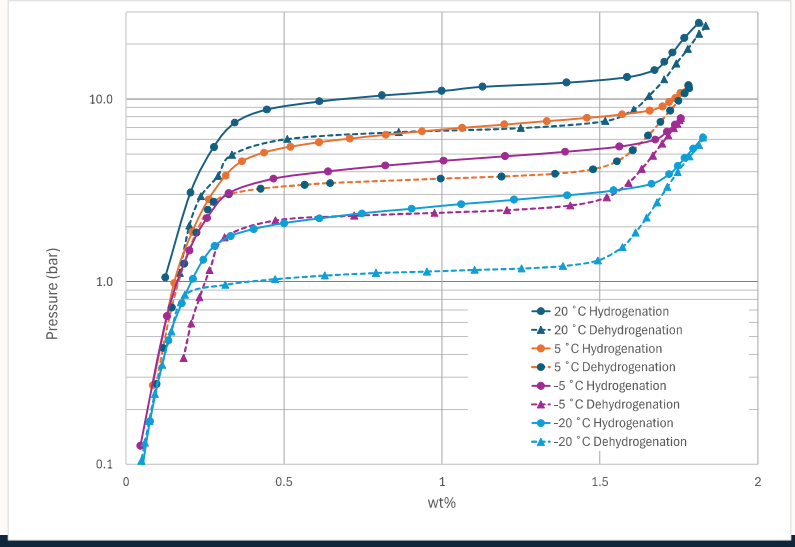
Feeding a 5 kW Fuel cell prediction with 2 door openings every 2 h

Experimental Validation of New Materials





- Bespoke Sievert's apparatus is designed to fit the gap between the liquid nitrogen and above-ambient temperature range
- Operating temperature range
  - -75°C to +180°C.
    - Achieved through climatic chamber control, with dual pressure transducers (0-2 Bar, 1-100 Bar)

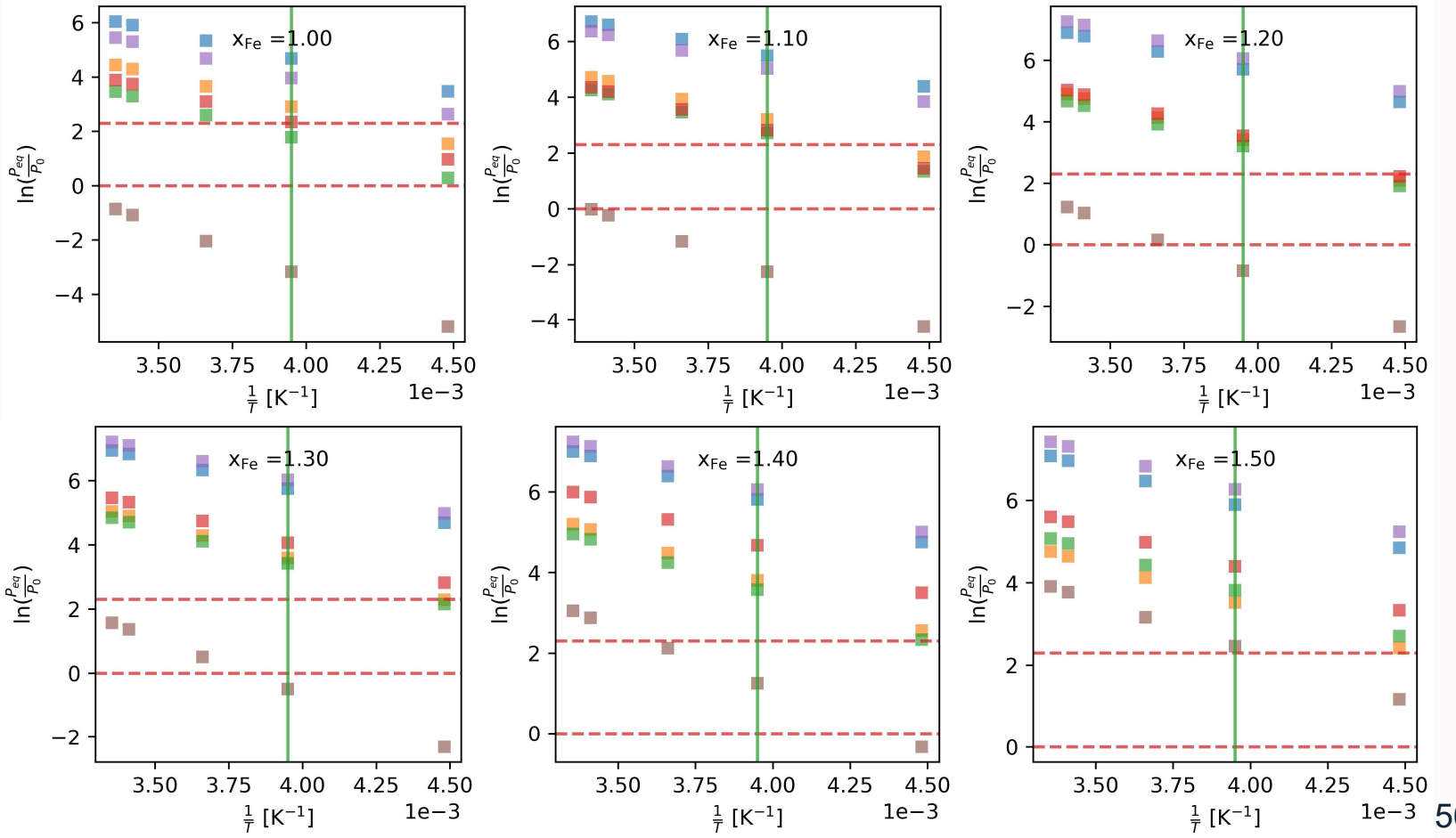


H2Cool composition design using machine learning

Temperature at green line: -20 °C, pressure bounds: (1,

$Ti_{0.8}Zr_{0.2}Fe_{2-x}M_x$ alloys

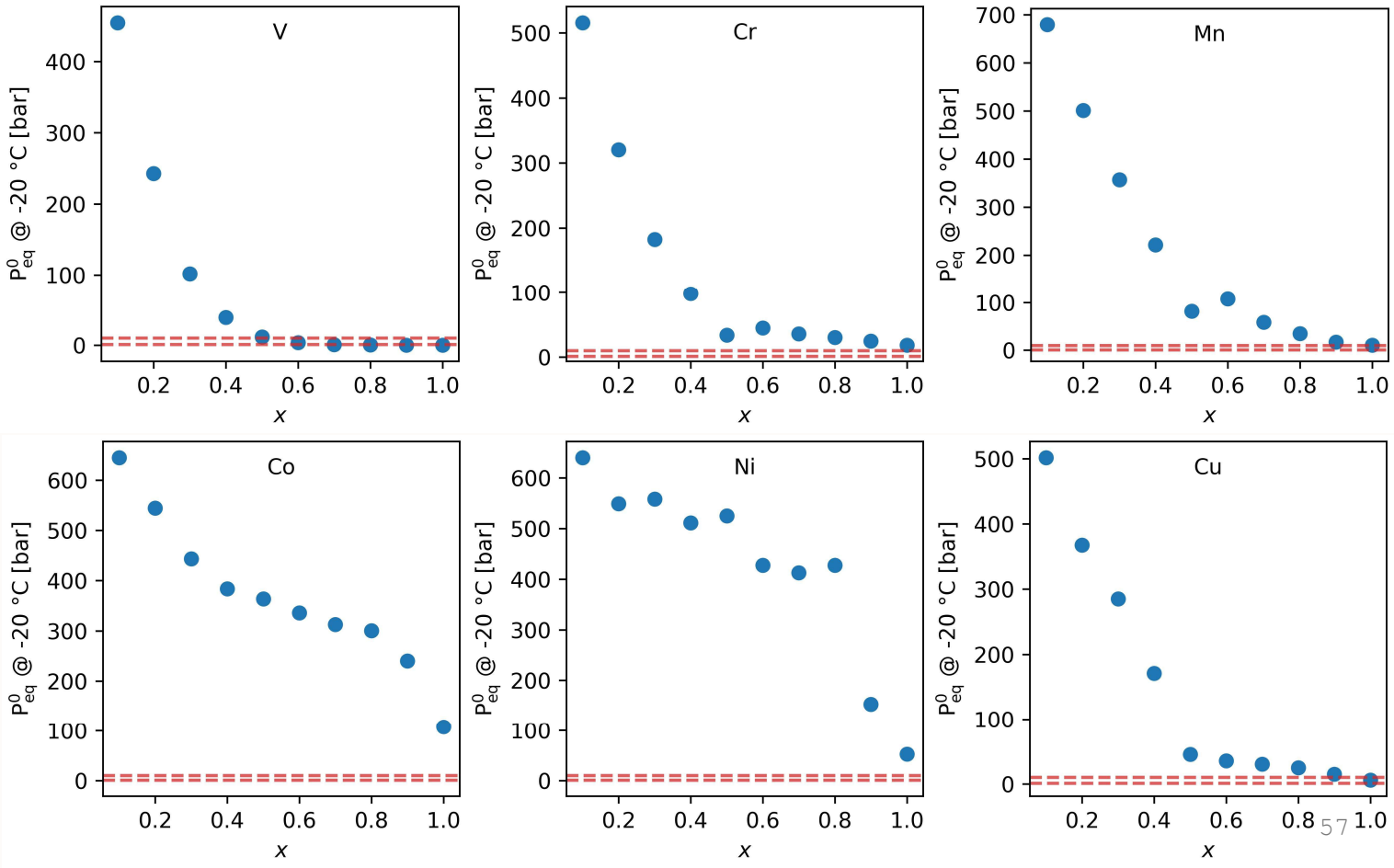
$Ti_{0.8}Zr_{0.2}Fe_{1.0}Cu_{1.0}$ and $Ti_{0.8}Zr_{0.2}Fe_{1.4}V_{0.6}$ meet the plateau pressure requirements



Composition design using machine learning

$Ti_{0.8}Zr_{0.2}Fe_{2-x}M_x$ alloys

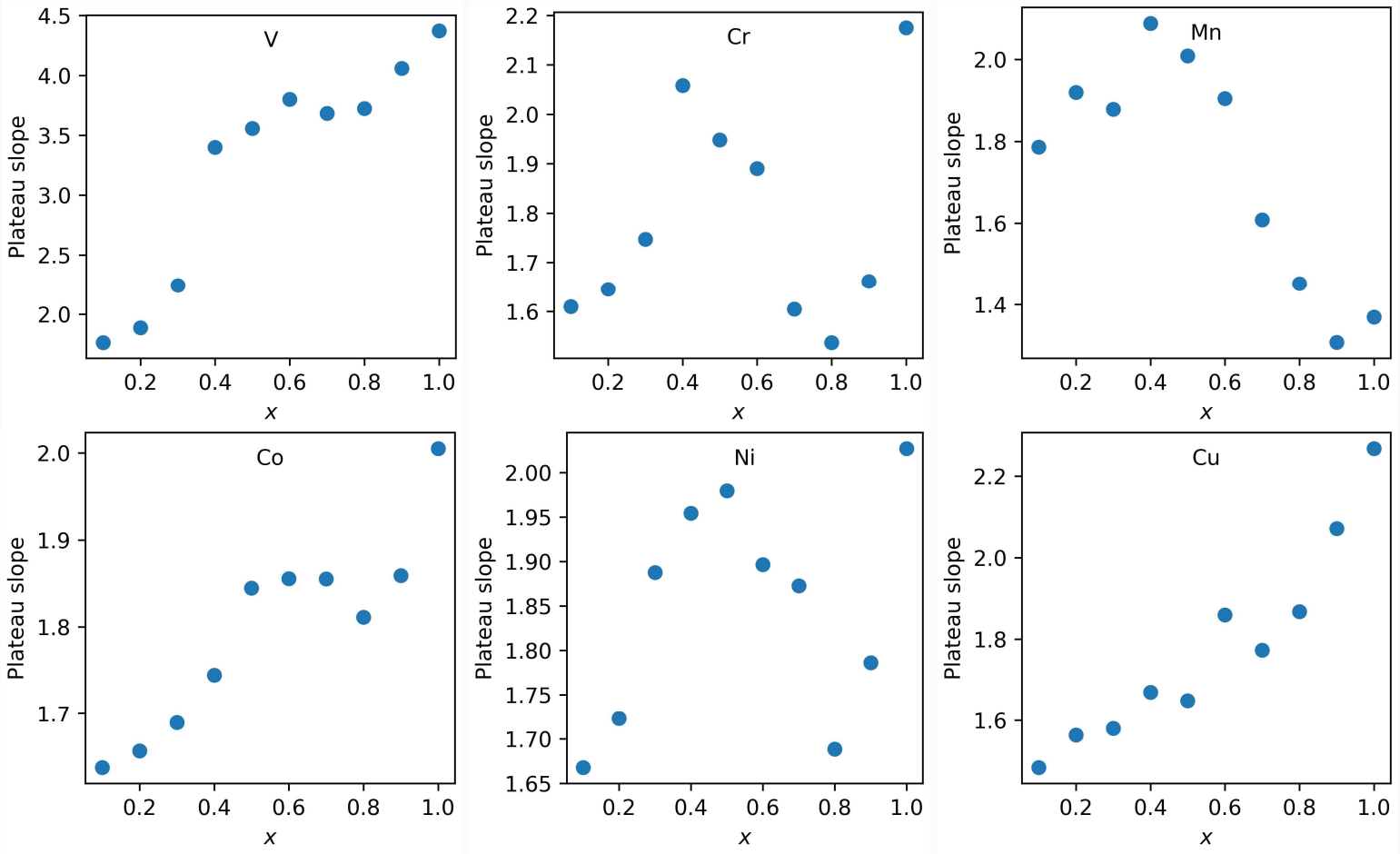
$Ti_{0.8}Zr_{0.2}Fe_{1.0}Cu_{1.0}$ and $Ti_{0.8}Zr_{0.2}Fe_{1.4}V_{0.6}$ meet the plateau pressure requirements



Composition design using machine learning

$Ti_{0.8}Zr_{0.2}Fe_{2-x}M_x$ alloys

$Ti_{0.8}Zr_{0.2}Fe_{1.0}Cu_{1.0}$ is a better choice in terms of plateau slope compared to $Ti_{0.8}Zr_{0.2}Fe_{1.4}V_{0.6}$



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H2Cool summary

- 1/8th scale validated
- ¼ scale being built with store and circulating fan at ends and simulated door openings
- Materials selection and synthesis and testing for -20 ˚C, 1 – 10 bar plateau pressure ongoing

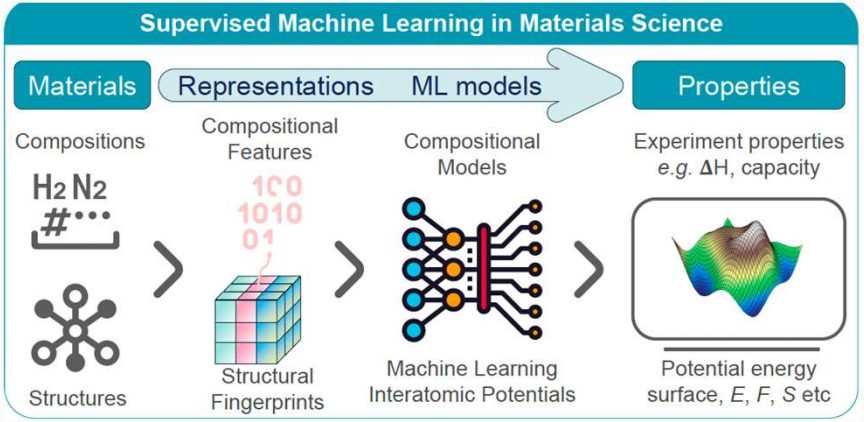
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More on Modelling

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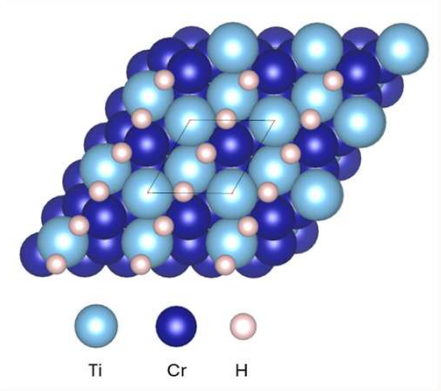
Computational and Data-Driven Modelling and Discovery of Metal Hydrides

Lei Lei, Matthew Witman, David Grant, Martin Dornheim, Sanliang Ling
Sanliang Ling



Ab Initio Modelling of the Kinetics of Hydrogen Absorption in $TiCr_2$ and $TiMn_2$ Surfaces and the Effect of Surface Substitutions

Sam Lines, David Grant, Sanliang Ling



Identified most stable facets of $TiCr_2$ and $TiMn_2$ in C14 (001) and C15 (111) phases. Substitutions were found to lower the kinetic barrier of the rate-limiting step

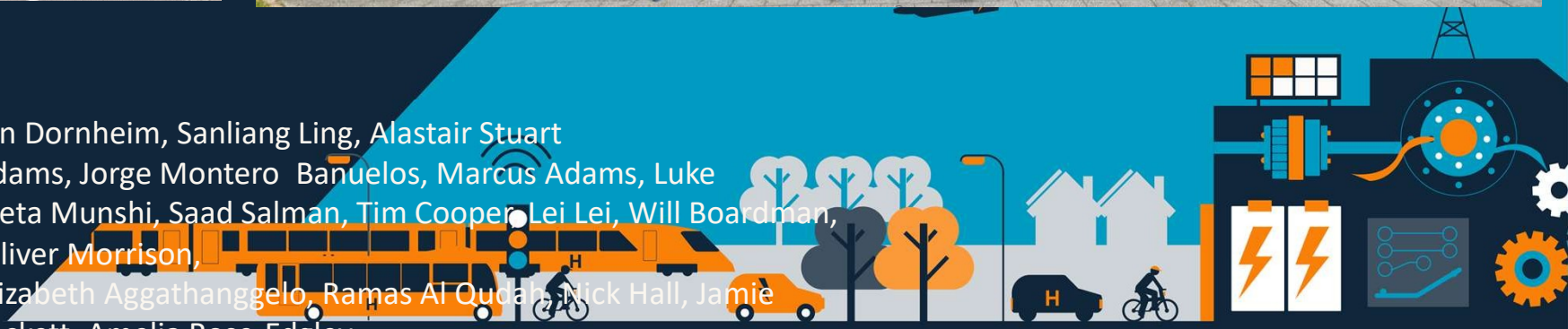
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UoN Hydrogen Research





Acknowledgements:
Academics: David Grant, Martin Dornheim, Sanliang Ling, Alastair Stuart
Researcher Fellows: Marcus Adams, Jorge Montero Banuelos, Marcus Adams, Luke Woodliffe, Drew Shephard, Sweta Munshi, Saad Salman, Tim Cooper, Lei Lei, Will Boardman, Navaratnarajah Kuganathan, Oliver Morrison,
PhD students: Andrew Gray, Elizabeth Aggathanggelo, Ramas Al Qudah, Nick Hall, Jamie Ramshaw, Sam Lines, Emily Blackett, Amelia Rose-Edgley



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Data distribution imbalance and extreme value prediction

Data:

Source: Sandia database + literatures
Properties: ΔH, ΔS, plateau pressure, capacity, plateau slope etc.

Data distribution imbalance:

Natural deviation from even distribution of properties

Challenges:

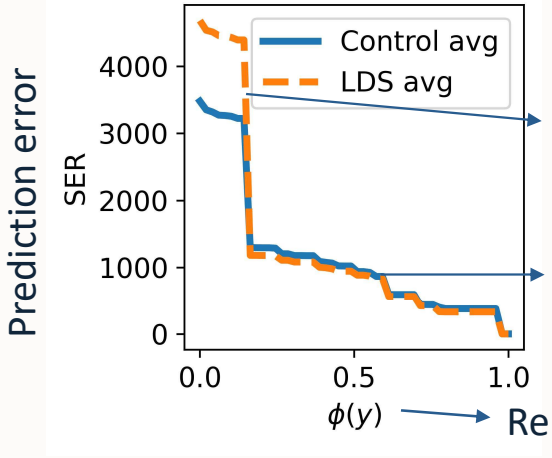
- Local overfitting
- Data selection sensitive
- Poor accuracy at extremes

Method

Ensemble of models implemented with algorithm methods to deal with data distribution imbalance

Materials discovery is often looking at extreme properties: e.g. low desorption enthalpy with low plateau slope for metal hydride compressors

	Overall error ↑ MAE	"Error" at extremes ↑ SERA
Control	3.70	162.95
LDS	3.79	148.77



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Five components

Empirical rules of $Ti_{0.8}Zr_{0.2}Fe_{2-x-y}Ni_xM_y$ alloys

M = Mn

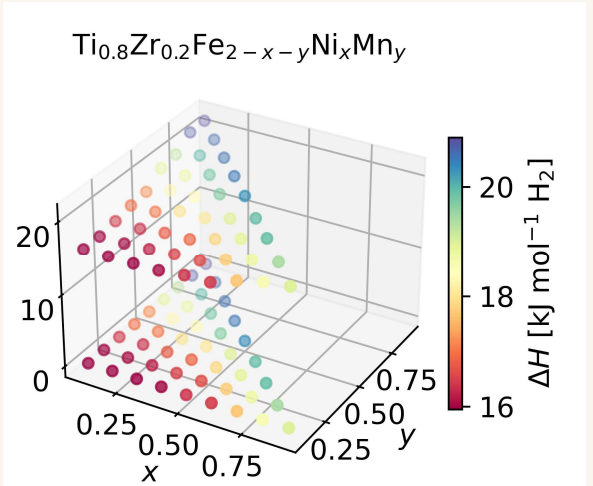
lnP and ΔH linear in limited range

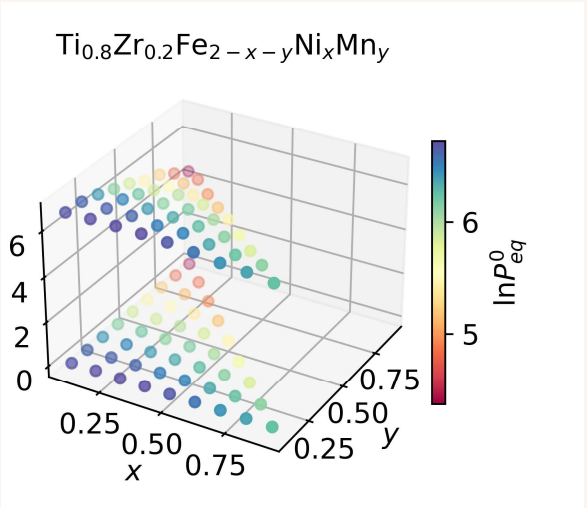
Concave ΔH, convex lnP

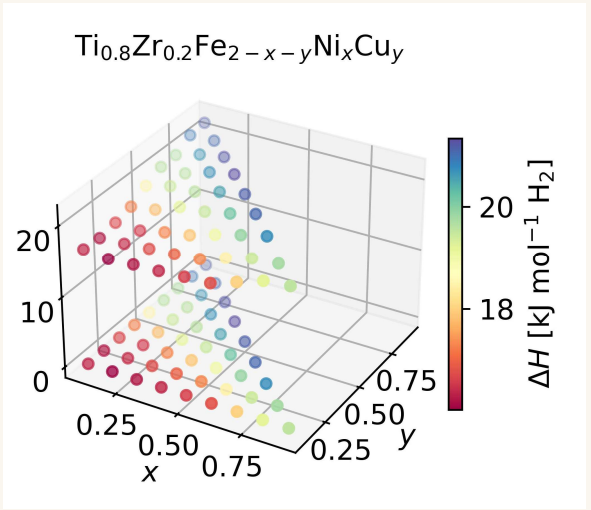
M = Cu

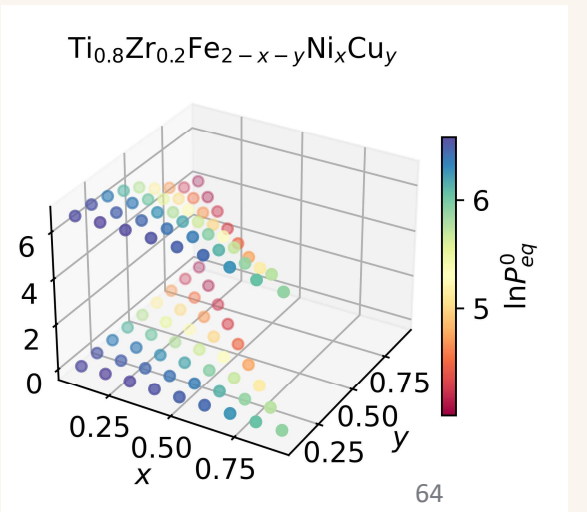
lnP and ΔH linear in limited range

Concave ΔH, convex lnP









Summary

- Structural analysis confirmed the formation of difference phases of $LiBH_4$.
- Ammoniate of hexagonal phase can also be stabilised.
- Halide-borohydride ammoniate may offer more structural stability than borohydride ammoniate.
- Local structure analysis agrees well with the proposed structure for halide-borohydride ammoniates – building blocks remain Li – $(BH_4)_{1-x}$ $(NH_3)_x$ – Li
- In-depth analysis suggests that a disordered structure in the presence of NH_3 maybe responsible for enhanced Li^+ conduction.
- This study confirms the key role of an ammoniated phase which may offer opportunities towards property tuning of several alkali or alkaline earth metal-hydride-nitride systems.

Borohydride-based ion conductors

J|A|C|S COMMUNICATIONS

Published on Web 01/02/2009

Halide-Stabilized $LiBH_4$, a Room-Temperature Lithium Fast-Ion Conductor

Hideki Maekawa,*,†,‡ Motoaki Matsuo,§ Hitoshi Takamura,† Mariko Ando,† Yasuto Noda,|| Taiki Karahashi,† and Shin-ichi Orimo§

ACS APPLIED MATERIALS & INTERFACES

www.acsami.org Research Article

Li-Ion Conductivity Enhancement of $LiBH_4 \cdot xNH_3$ with *In Situ* Formed Li_2O Nanoparticles

Wanying Zhao, Ruixue Zhang, Hongjiao Li, Yunsheng Zhang, Yao Wang, Chaoling Wu,* Yigang Yan,* and Yungui Chen

CHEMISTRY OF MATERIALS

pubs.acs.org/cm Article

Incorporation of Ammonia Borane Groups in the Lithium Borohydride Structure Enables Ultrafast Lithium Ion Conductivity at Room Temperature for Solid-State Batteries

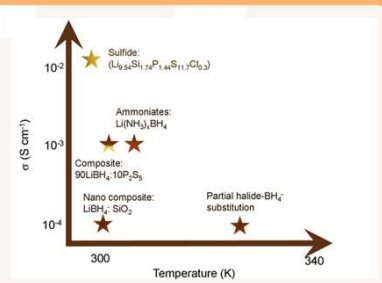
Huan Liu,¶ Zhuanghe Ren,¶ Xin Zhang, Jianjiang Hu, Mingxia Gao, Hongge Pan, and Yongfeng Liu*

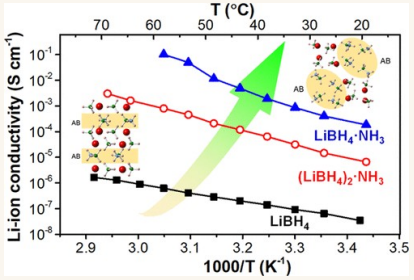
J|A|C|S JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Cite This: *J. Am. Chem. Soc.* 2019, 141, 5640−5644 Communication pubs.acs.org/JACS

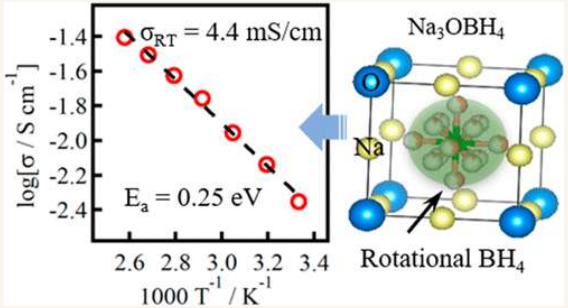
Rotational Cluster Anion Enabling Superionic Conductivity in Sodium-Rich Antiperovskite Na_3OBH_4

Yulong Sun,† Yuechao Wang,‡ Xinmiao Liang,§ Yuanhua Xia,|| Linfeng Peng,† Huanhuan Jia,† Hanxiao Li,‡ Liangfei Bai,|| Jiwen Feng,§ Hong Jiang,*,‡ and Jia Xie*,†





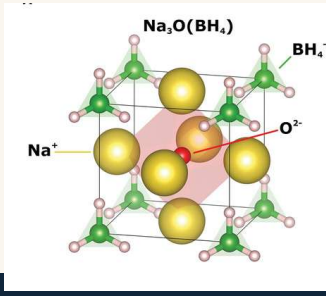
Chem. Mater. **2020**, *32, 2, 671-678*

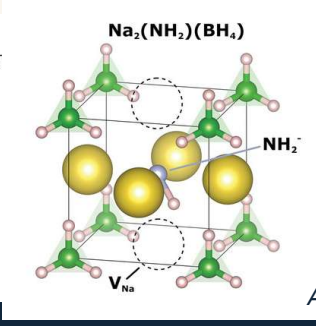


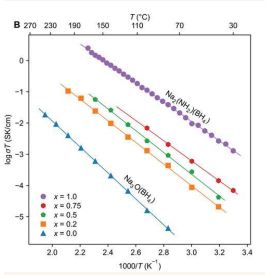
J. Am. Chem. Soc. **2019**, 141, 5640-5644

$M_n(NH_2)(BH_4)$ in the presence of NH_3

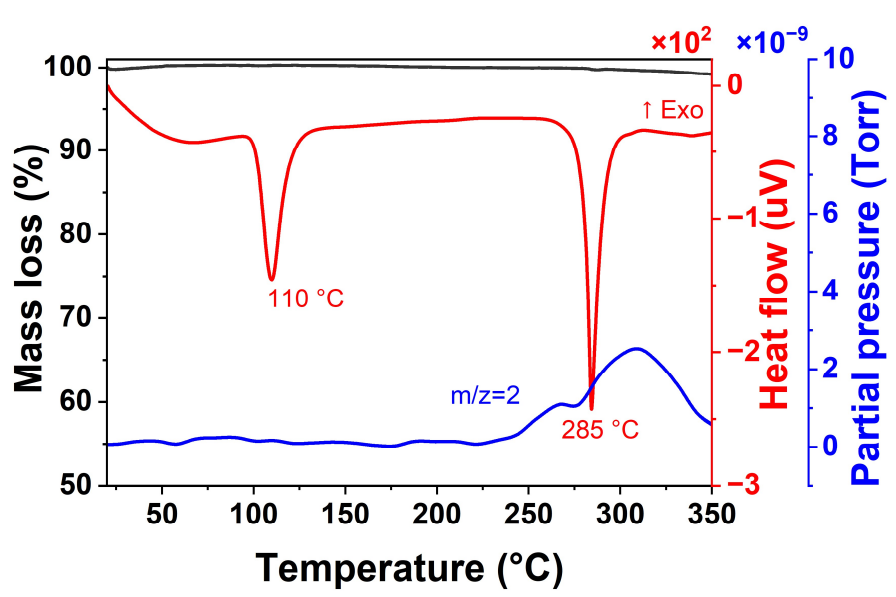
Organometallics **2022**, 41, 20, 2823-2832



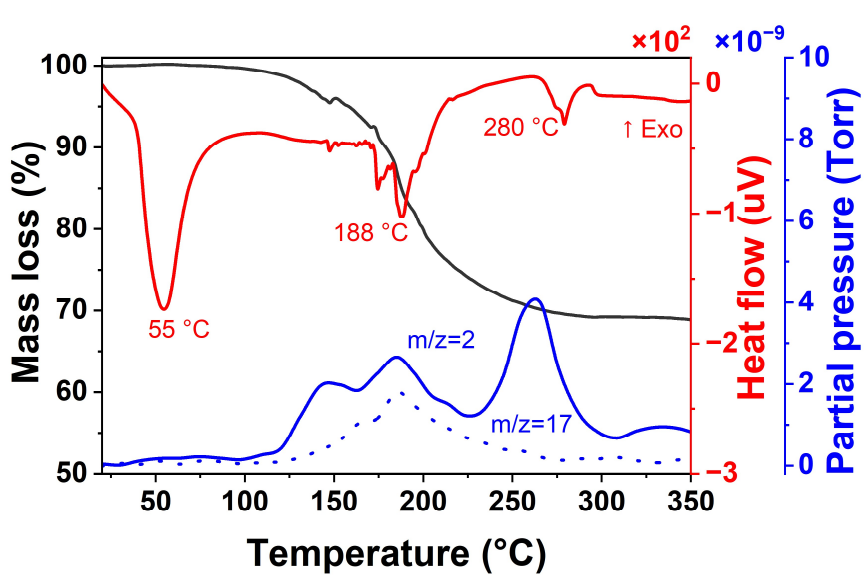




Hydrogen and ammonia release for $LiBH_4$ and $LiBH_4(NH_3)$



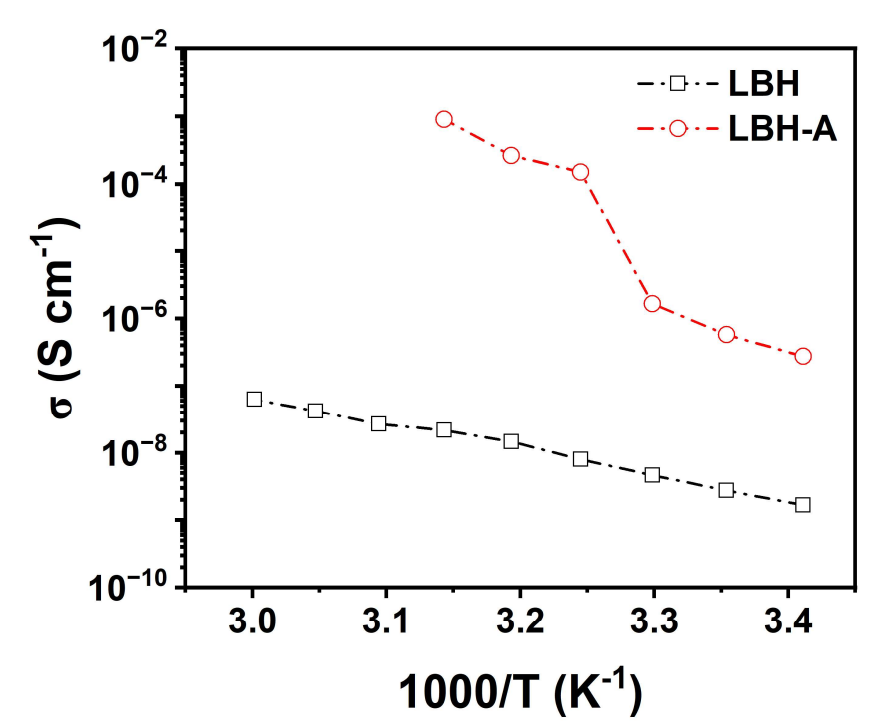
$LiBH_4$

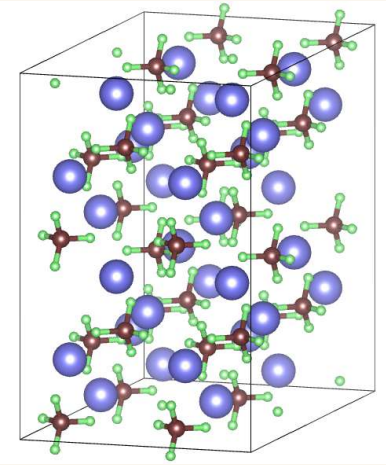


$LiBH_4(NH_3)$

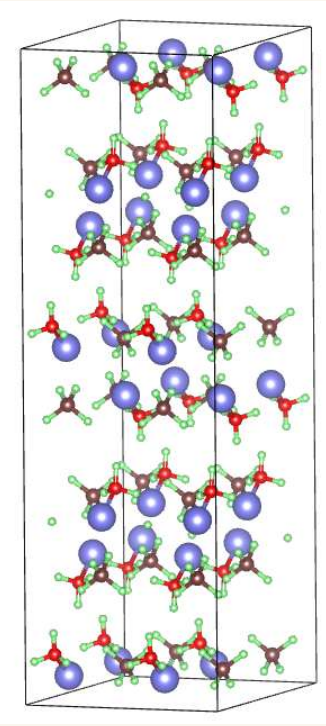
Ionic conduction – the ammonia effect

The $LiBH_4$ and $LiBH_4(NH_3)$ systems



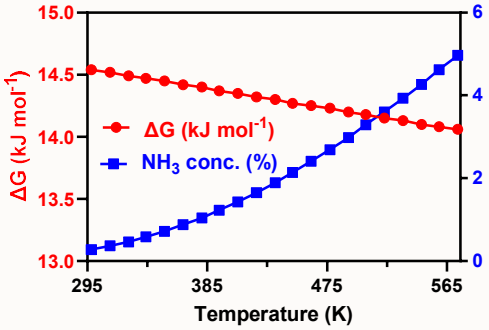


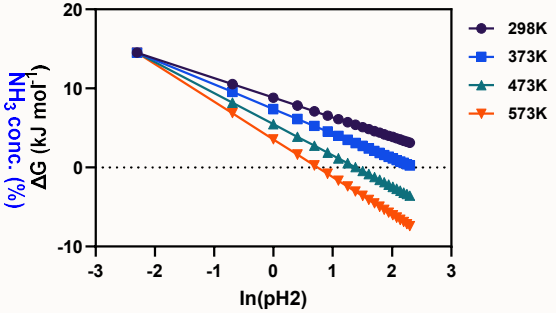
$LiBH_4$

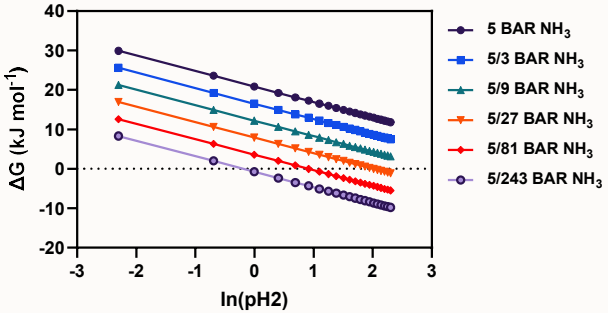


$LiBH_4(NH_3)$

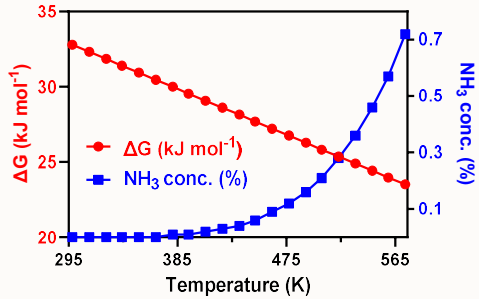
Faster kinetics
But low capacity

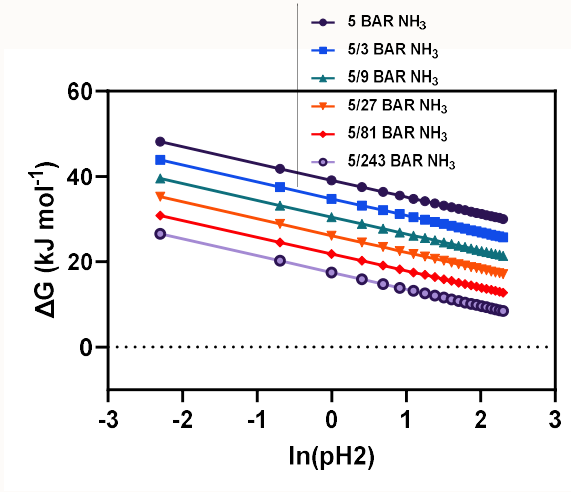


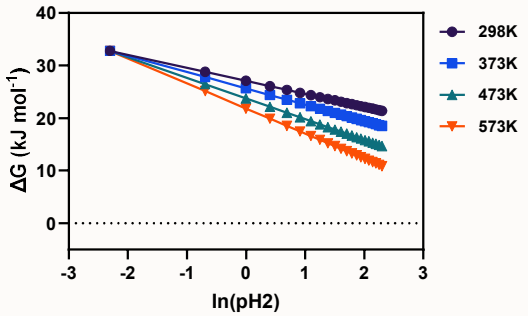




$$KH + NH_3 \overset{\Delta}{\leftrightarrow} KNH_2 + H_2$$







$$LiH + NH_3 \overset{\Delta}{\leftrightarrow} LiNH_2 + H_2$$

Slow kinetics

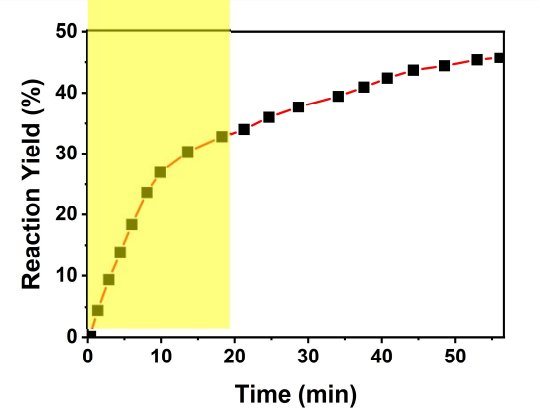
$$LiNH_2 + H_2 \overset{\Delta}{\leftrightarrow} LiH + NH_3$$

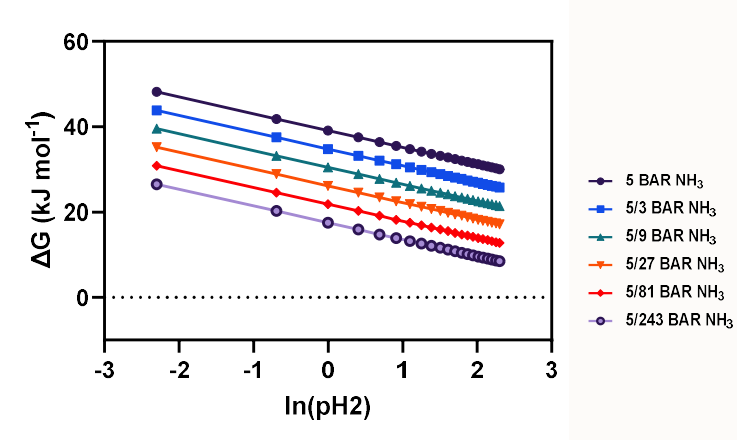
Not favourable!

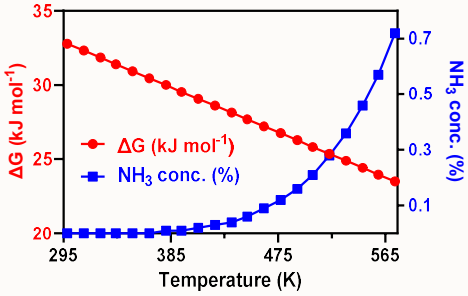
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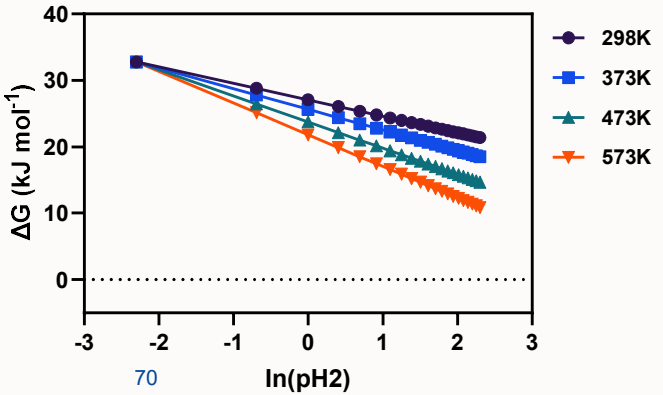
LiH-NH_3 System

Ideally









$$LiH + NH_3 \overset{\Delta}{\leftrightarrow} LiNH_2 + H_2$$

Slow kinetics!

$$LiNH_2 + H_2 \overset{\Delta}{\leftrightarrow} LiH + NH_3$$

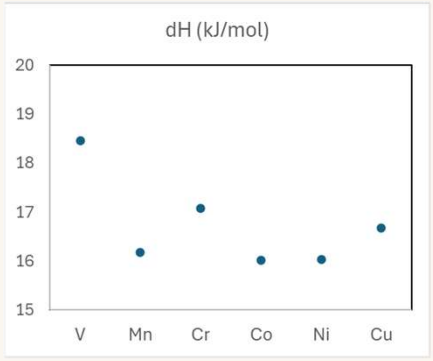
Not favourable!

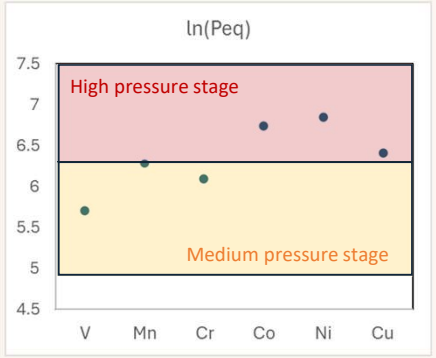
Element substitution

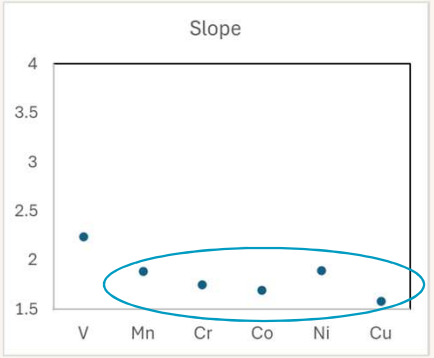
$Ti_{0.8}Zr_{0.2}Fe_{2-x}M_x$

M= Cu, Co, Ni, Cr, Mn, V

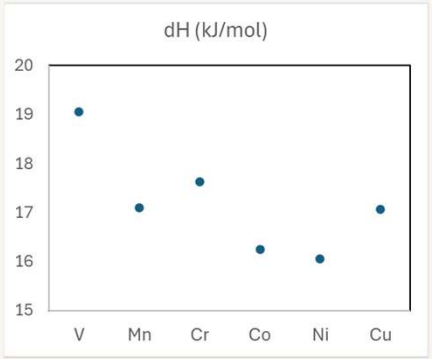
X=0.3

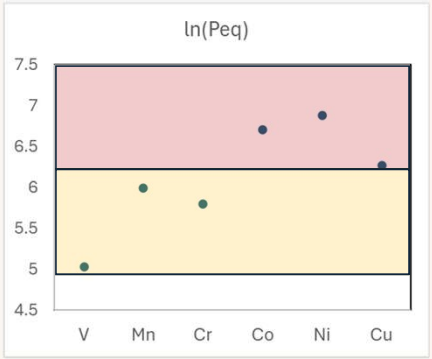


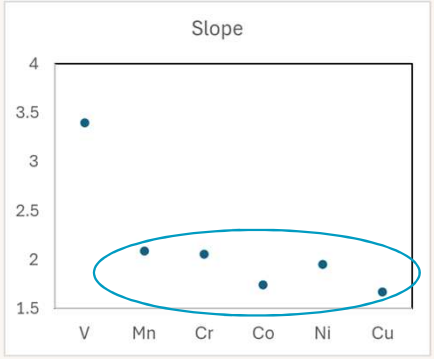




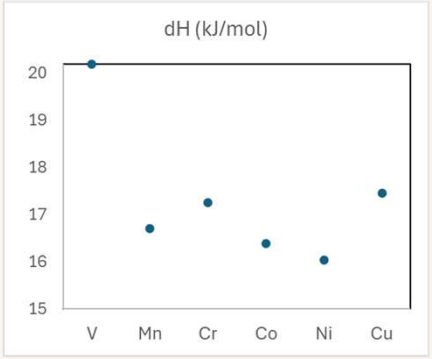
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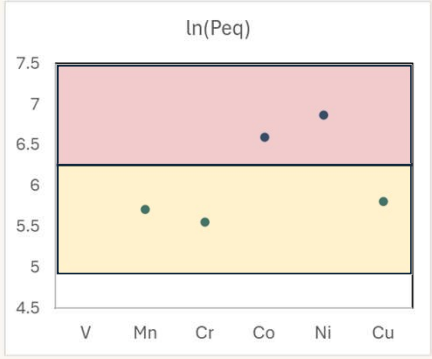


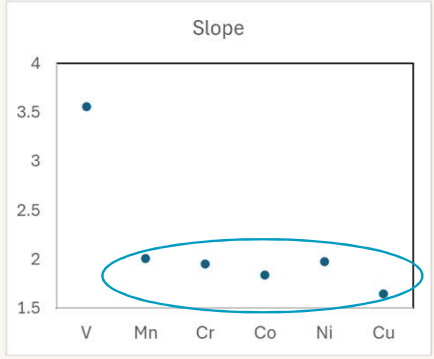




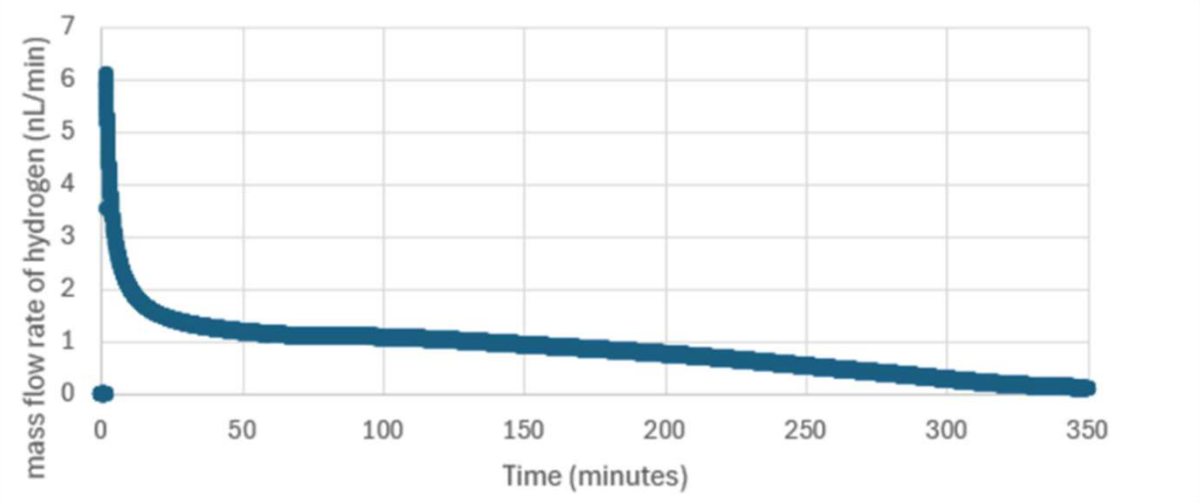
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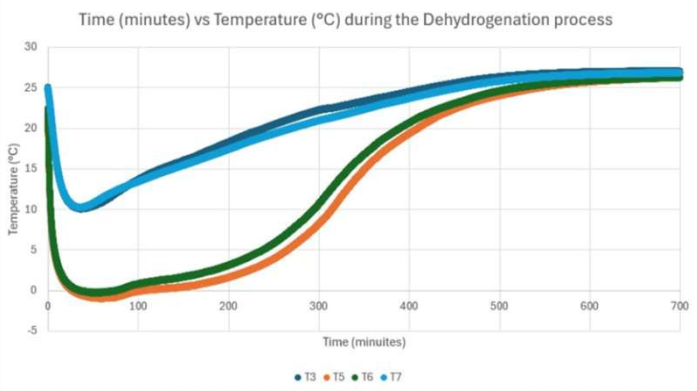






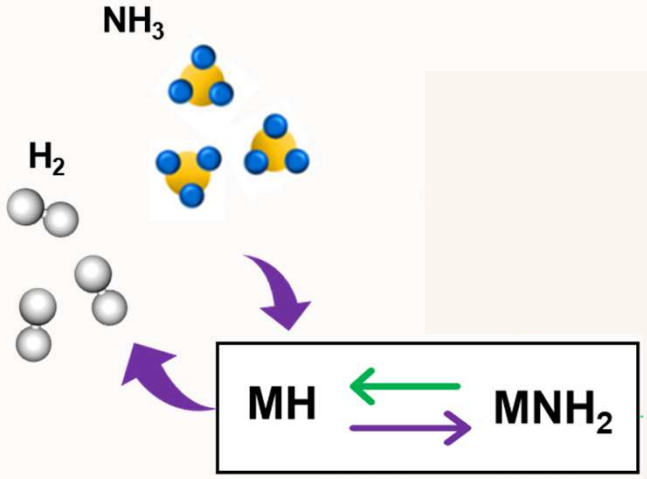
1/8th protype:
Example free flow and tank temperatures





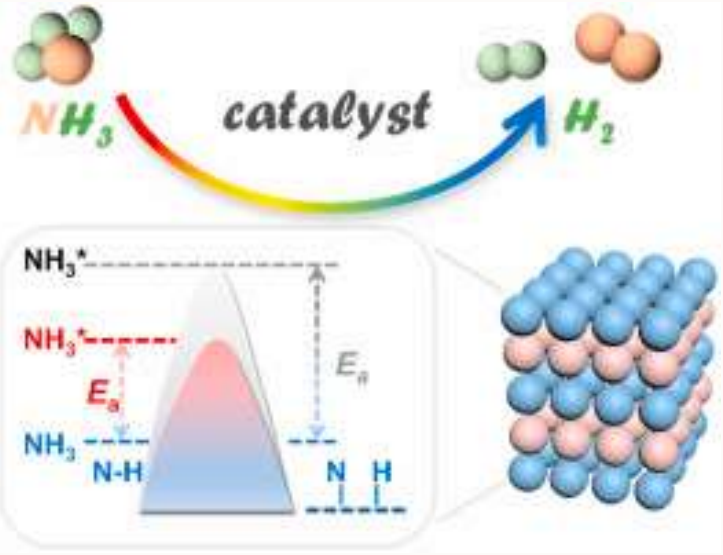
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MH-NH_3 systems for hydrogen production – Other routes ?



$$LiH + NH_3 \overset{\Delta}{\leftrightarrow} LiNH_2 + H_2$$

(RT, ~8.1 mass% H_2)



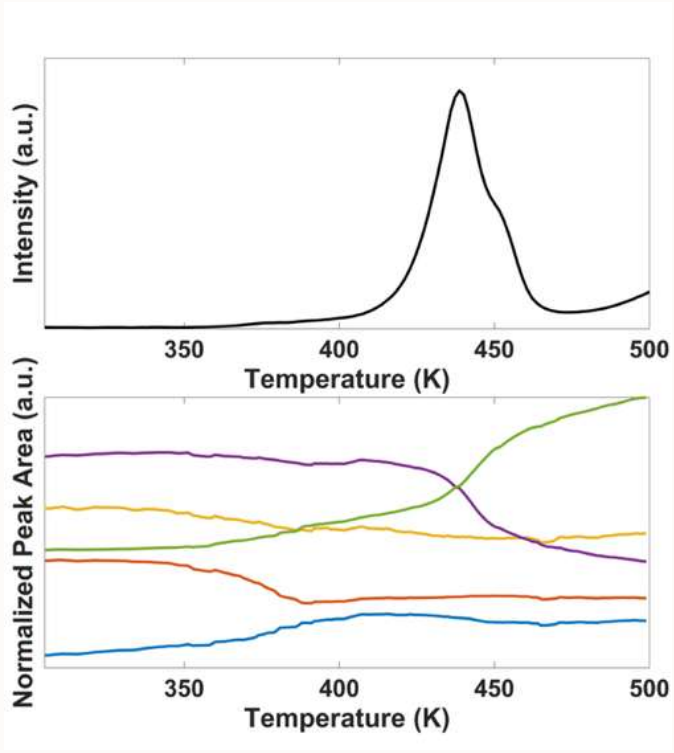
Renew. Sustain. Energy Rev., **2022**, 169, 112918.

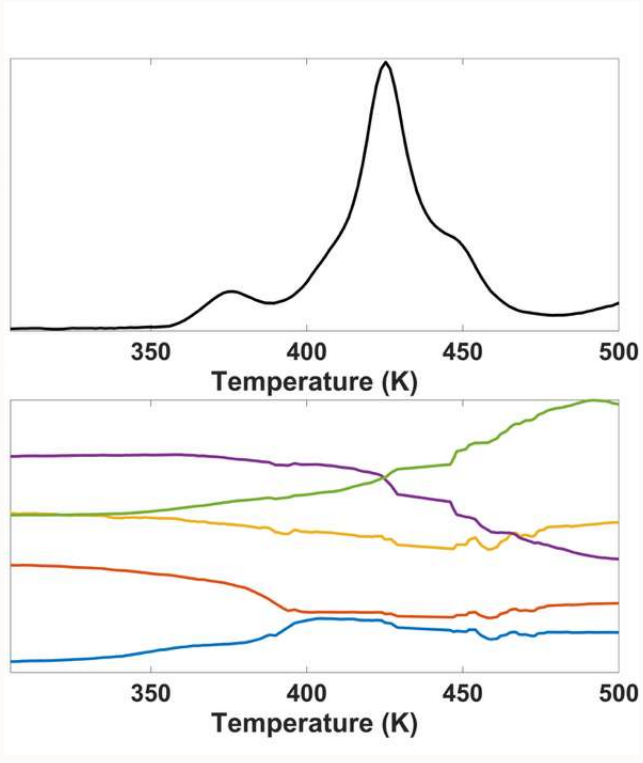
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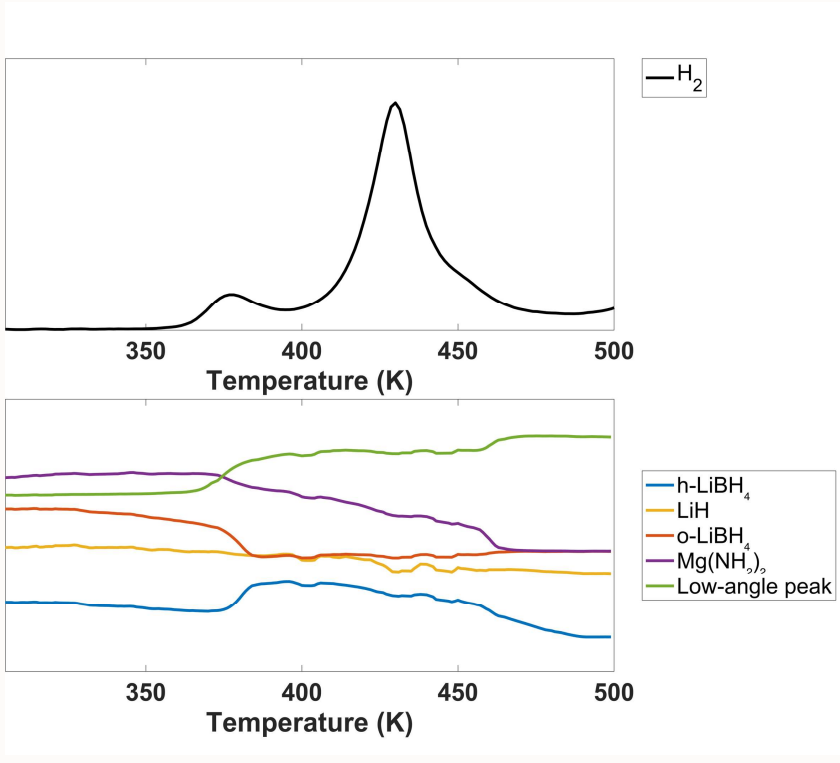


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MS data







6:9:12

6:9:18

6:9:24