Pacific Northwest NATIONAL LABORATORY

HyMARC Hydrogen Materials Advanced Research Consortium

PNNL Effort in HyMARC

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Pacific Northwest National Laboratory

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Overview

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Timeline

- **Phase 1: 10/1-15 to 9/30/18**
- **Phase 2: 10/1/18 to 9/30/22**
- **Project continuation determined annually by DOE**

Budget PNNL

FY18 Phase 1 $800K
FY18 Phase 2 $1,050K
FY19 Phase 2 $400K*
***through 3/31/19**

Barriers

- **General:**
- A. Cost; B. Weight and Volume; C. Efficiency; E. Refueling Time
- **Reversible Solid-State Material:**
- M. Hydrogen Capacity and Reversibility;
- N. Understanding of Hydrogen Physi- and Chemi- sorption; O. Evaluation Facilities.
- **Hydrogen Carriers**

Partners/Collaborators

- NREL - Tom Gennett, Phil Parilla
- NIST - Craig Brown, Terry Udovic
- LBNL - Jeff Long, Hanna Breunig
- HyMARC - Brandon Wood, Vitalie Stavila
- Hawaii – Craig Jensen
- DICP – P Chen, T He
- Geneva – H Hagemann, A Gigante
- AIST – Q Xu, Y Himeda, H Kawanami
- KIST – Hyangsoo Jeong, Chang Won Yoon
- Erlangen Nuremberg – K Müller

We build upon the guidance provided by Hydrogen Storage Centers of Excellence

PNNL leverages unique capabilities to assist material developers:

- Solid-state in-situ high-pressure variable-temperature ^{11}B,^{13}C,^{15}N NMR (to identify key intermediates involved in the release and uptake of H_2),
- Solid-state low temperature ^{1}H and ^{2}H NMR (5 – 300 K) to investigate physi-sorption of H_2, ultimate goal to validate > $2H_2$/metal site.
- Variable pressure reaction calorimetry to experimentally determine enthalpy of H_2 addition in solid and liquid hydrogen stores (high pressure cells unique to PNNL)
- Characterization of liquid carriers: kinetics (constant P and V reactors to monitor pH, pressure, and temperature); spectroscopy (in-situ NMR, reactIR, LCMS); thermodynamics (calorimetry, DSC/TGA/MS and PCT); gas purity (RGA, IR, GC)

Goal of Consortium:

- to assist materials developers to measure (and validate) critical properties to increase energy density
- to develop and enhance FCTO hydrogen storage **core characterization capabilities**
- to **validate** *new concepts* for input into predictive models that will accelerate progress of materials developers and improve approaches to onboard H_2 storage and hydrogen carriers

Collaborations

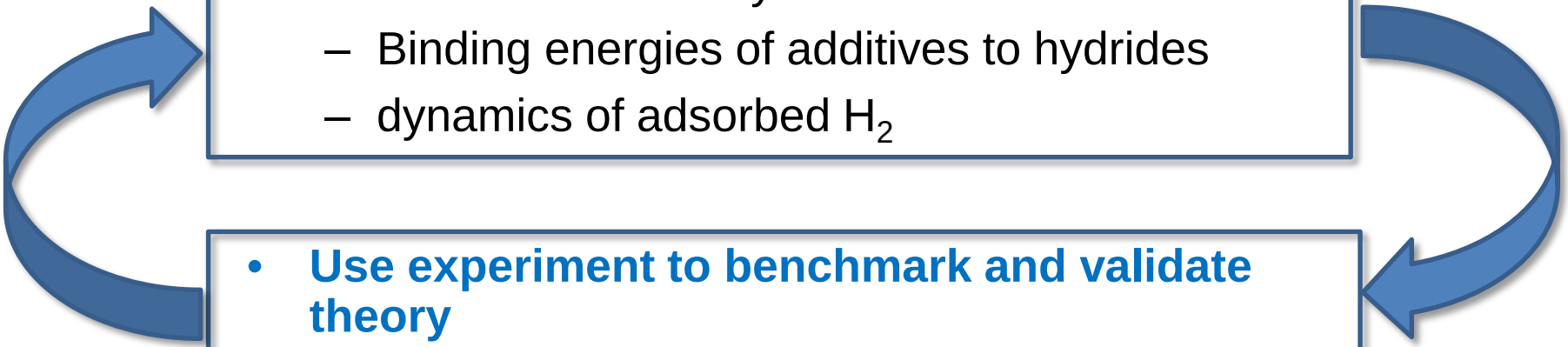
accelerate discovery of process through leveraged expertise

- Hawaii – PCT cycling $Mg(BH_4)_2$ (Craig, Phuong, Sunil)*
- KIST – Physiochemical properties formate (Hyangsoo, Chang)*
- HI ERN – chemical compression formic acid (Karsten)**
- AIST – High pressure NMR *in–situ* solution NMR (Qiang, Yuichi)**
- Geneva - ^{11}B NMR, calorimetry unsolvated $Mg(B_3H_8)_2$ (Hans, Angelina)
- DICP - Reaction calorimetry ΔH_{H2} (aqueous organics) (Teng, Ping)*
- NREL – ^{11}B NMR of BH_4 compounds (Tom G, Bob, Noemi, Steve)
- NIST – NVS of $THF_XMg(^{11}BD_4)_2$ complexes (Mira, Terry)*
- LBNL – Low temperature ^2H NMR Mg-dobdc (Hiro, Jeff)
- SNS – INS of FLPs (Timmy, Luke, Martin)
- LLNL – interface of materials & chemistry in complex hydrides (Brandon)

***** joint publications (** two publications)

Dynamic link between theory & experiment

- **Use theory to guide experiment and interpret complex results**
  - Predict key intermediates and products based on thermodynamics
  - Binding energies of additives to hydrides
  - dynamics of adsorbed H_2



- **Use experiment to benchmark and validate theory**
  - Propose and test chemical reaction pathways
  - NMR to follow evolution of H_2 release pathways (key intermediates and products)
  - Measuring thermodynamics and kinetics of H_2 uptake and release

Overview – work structure - phase 2

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- **Task 1 Sorbents**
  - 1.A: Enthalpy / Entropy (LBNL, NREL, PNNL) Bowden, Lipton, Ginovska
- **Task 2 Hydrides**
  - 2.C.2 Modeling of B-B bond activation (SNL, LBNL, LLNL, PNNL) Ginovska
  - *2.C Activation of B-B and B-H Bonds (SNL, LBNL, NREL, PNNL) Autrey*
- **Task 3 Carriers**
  - 3.A Alternate electrochemical approaches to produce hydrogen carriers (Wiedner)
  - 3.B.2 Aqueous organic carriers (PNNL, DICP) Autrey, Brooks
  - 3.B.3 Formate/Bicarbonate cycle (PNNL, KIST) Grubel
  - *3.C.1 Magnesium borohydride melts (PNNL, NREL) Autrey*
  - *3.D.2 Porous liquids as hydrogen carriers (NREL, PNNL, LBNL, LLNL) Ginovska, Karkamkar*
  - *3.G.1 Frustrated Lewis acid-base pairs (PNNL, NREL) Bowden, Ginovska*
- **Task 4 Capability Development**
  - *Hydrogen Carrier Characterization (PNNL) Karkamkar, Grubel*
  - *Advanced NMR Spectroscopy (PNNL) Lipton, Bowden*
- **Task 5 Seedling support**
  - *Technologist with NMR expertise (PNNL) Lipton, Bowden*
  - *Technologist with Liquid H_2 Carrier expertise (PNNL) Grubel, Karkamkar, Autrey*
- **Task 6 Data Hub**
  - *support (PNNL) Sivaraman*

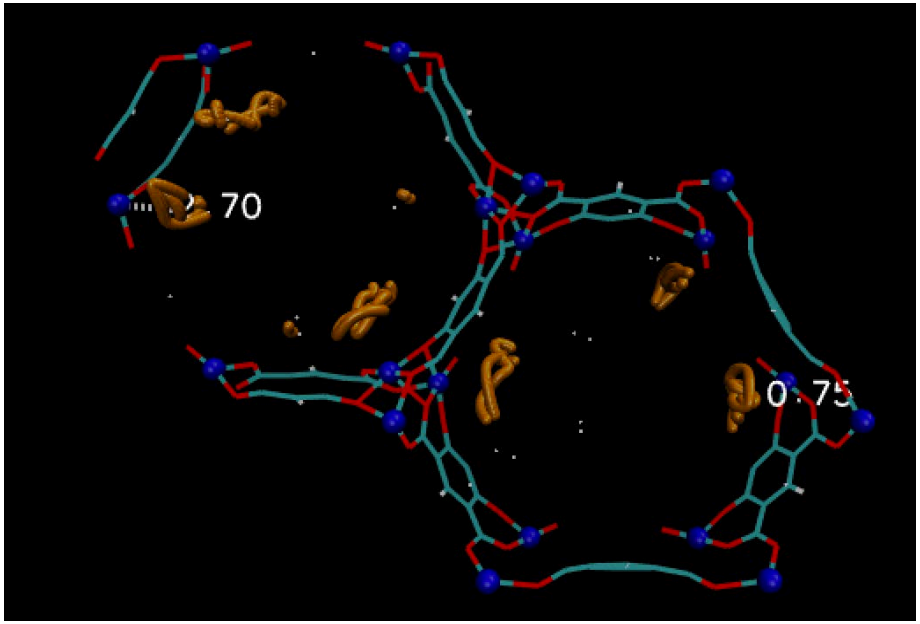
Sorbents. 1.A: Enthalpy / Entropy vs temperature

Bojana Ginovska

Enthalpic (ΔH) and Entropic (ΔS) contributions in solid state systems can be accounted for using:

1. *Harmonic or quasi-harmonic approximation, where frequencies are calculated from an optimized minimum energy structure (CP2K, VASP and Phonopy)*
2. *Ab initio molecular dynamic simulation (AIMD), where the frequencies are calculated from trajectories propagated over time, capturing non-harmonic effects (CP2K)*

AIMD simulation of H_2 movement in a CP2K using DFT showing dynamics 75 K.

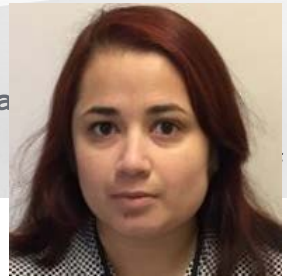


Orange spaghetti plot are H_2 within 3.5 Å of cobalt cation in dobdc, showing H_2 dynamics.

Take home: Combining theory (AIMD) and experiment (NMR) will provide insight into changes in *ΔS* and *ΔH* with temperature

Accomplishments using theory to down select pathways

Hydrides. 2.B Modeling B-B bond activation



Iffat Nayyar

Take home: Compare thermodynamics for > 20 different pathways to and from $B_{10}H_{10}$. Provide insight into the most likely pathways.

Are the key intermediates:

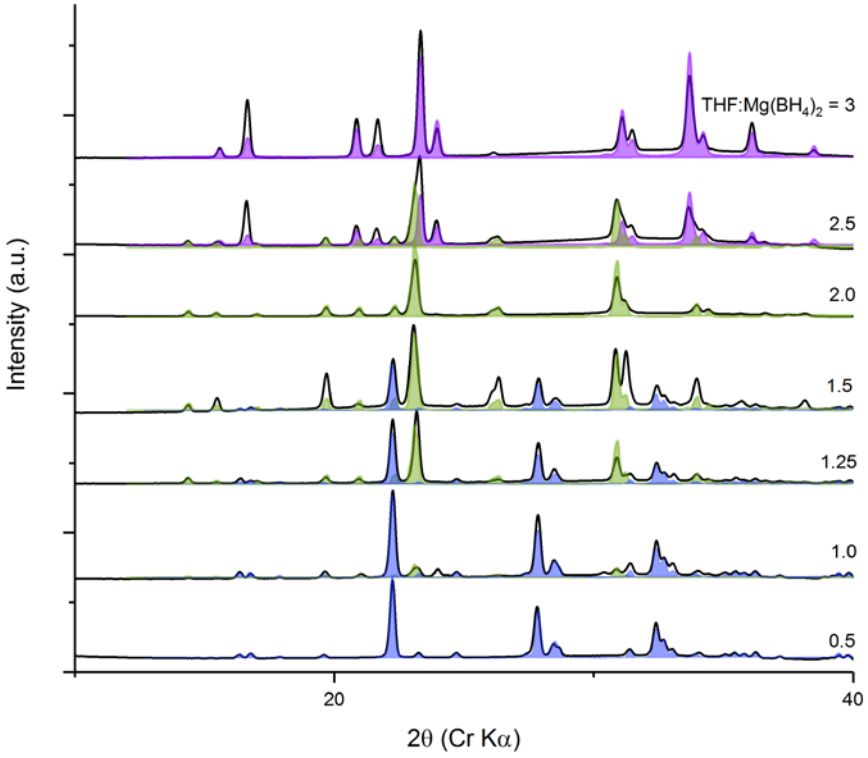
$B_2H_6^{2-}$ (need to activate $H_2B\text{-}BH_2$ bond) or $B_2H_7^-$ (need to stabilize BH_3)

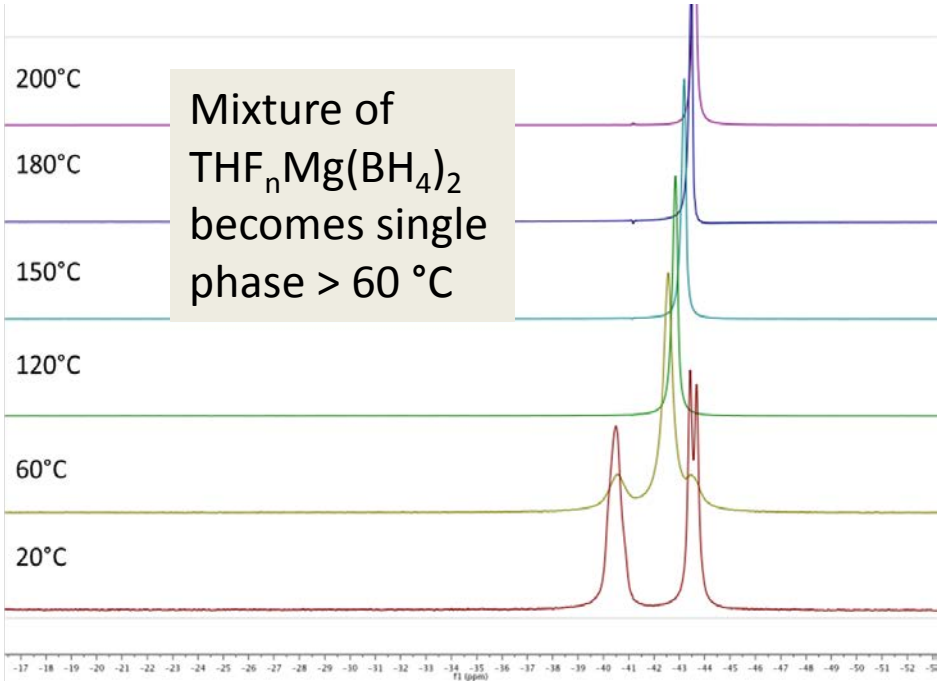
Reaction Path (1)	ΔE_{static}	ΔH_{vib}	ΔH^t_{vib}	ΔG^t_{vib}	ΔS^t_{vib}
	T = 0K		T = 300K		
	kJ/mol rxn				J/mol rxn K
	$Mg(BH_4)_2 \rightarrow MgB_2H_6$				
(1) $Mg(BH_4)_2 \rightarrow MgB_2H_6 + H_2$	66 (66)	47	49	22	93
	$MgB_2H_6 \rightarrow Mg(B_3H_8)_2$				
(2) $MgB_2H_6 + \frac{1}{3}H_2 \rightarrow \frac{1}{3}Mg(B_3H_8)_2 + \frac{2}{3}MgH_2$	52 (155)	52 (156)	50 (151)	61 (184)	-36 (-109)
(3) $6MgB_2H_6 + 4H_2 \rightarrow Mg(B_3H_8)_2 + 3Mg(BH_4)_2 + 2MgH_2$	-40 (-10)	16 (4)	4 (1)	120 (30)	-388 (-97)
(4) $4MgB_2H_6 + 2H_2 \rightarrow Mg(B_3H_8)_2 + Mg(BH_4)_2 + 2MgH_2$	90 (45)	110 (55)	102 (51)	162 (81)	-202 (-101)
(5) $2MgB_2H_6 + Mg(BH_4)_2 \rightarrow Mg(B_3H_8)_2 + 2MgH_2$	221	203	200	205	-16

Hydrides. 2.C Activation of B-B and B-H Bonds

Mark Bowden

Take home: Synthesis of THF adducts leads to a mixture of species – but they all melt and end up as a 'single' amorphous phase.





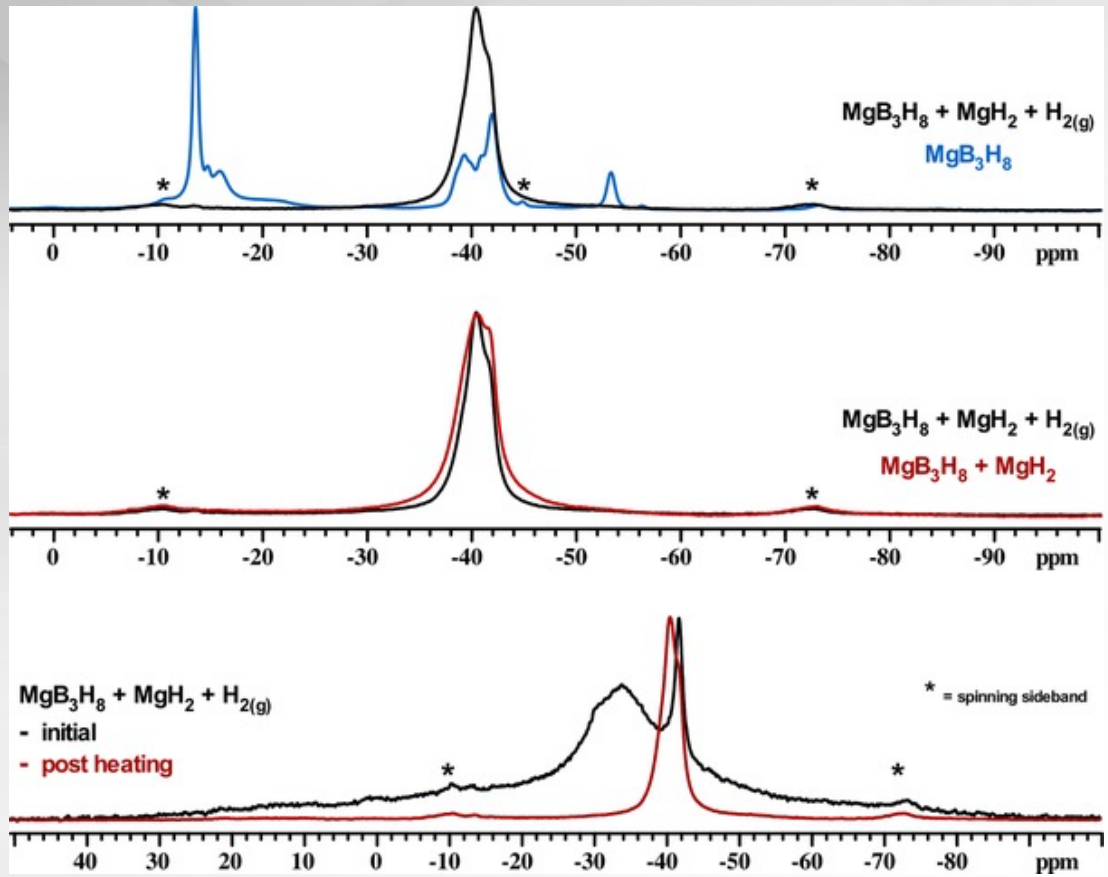
- purple n = 3, but discovered two new phases identified green n = 2, blue n = 2/3

Regeneration of BH_4 from ***solvent free*** $Mg(B_3H_8)_2$

Hydrides. 2.C Activation of B-B and B-H Bonds

Andy Lipton

Do you need weeks at 80 bar and 200 °C to regenerate BH_4 from solvent free B_3H_8? ***No, hours at 100 °C and 50 bar – but need MgH_2***



MgH_2 and H_2 present lead to the expected BH_4 as the major product. In the absence of MgH_2 see additional boranes, e.g., $B_{12}H_{12}$

Before and after showing solvent free B_3H_8 conversion to BH_4

Can combine ***in-situ solid state NMR*** *with solution NMR to get a more accurate picture of key intermediates*

B_3H_8 Max H_2 density ca. 2.4 wt%

Accomplishments developing protocol to quantify intermediates in reversible pathways

Hydrides. 2.C Activation of B-B and B-H Bonds

Angelina Gigante

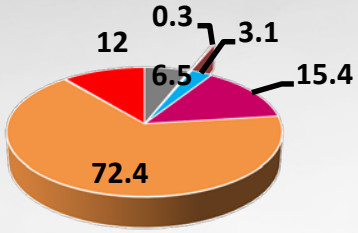
Liquid state ^{11}B NMR of $Mg(B_3H_8)_2+4MgH_2+H_2$ 85psi 200 °C

Take home:

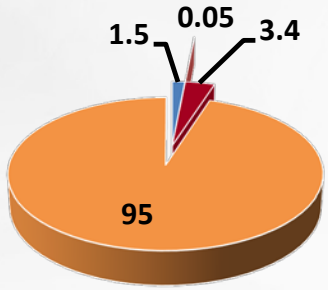
Solution NMR provides higher resolution to observe minor products

Different solvents provide different looks (stability and solubility of intermediates

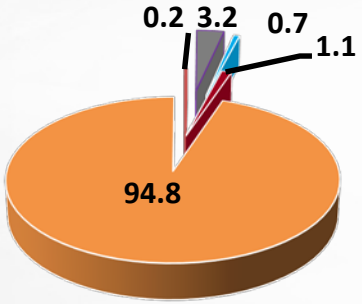
$Mg(B_3H_8)_2 + 4MgH_2 + H_2$



THF-D_2O

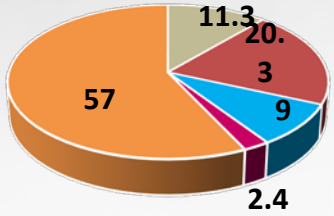


DMSO-d6

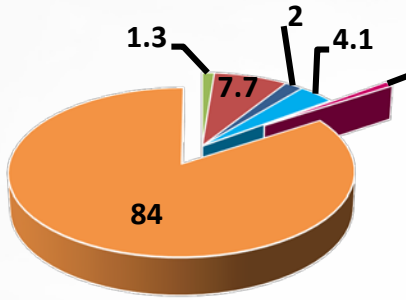


CD_3CN

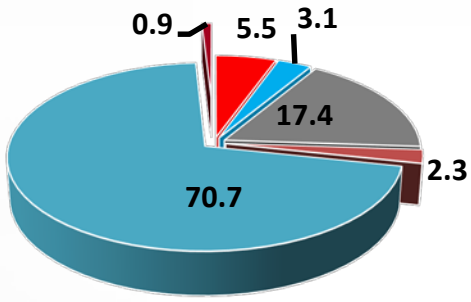
$Mg(B_3H_8)_2$



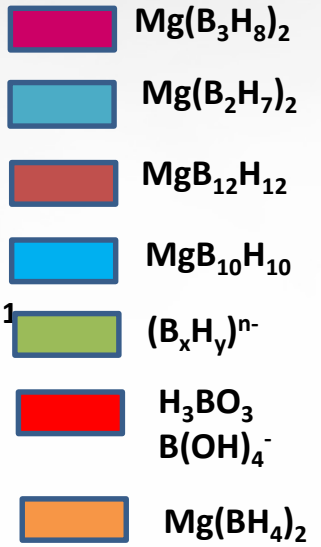
THF-D_2O



DMSO-d6



CD_3CN

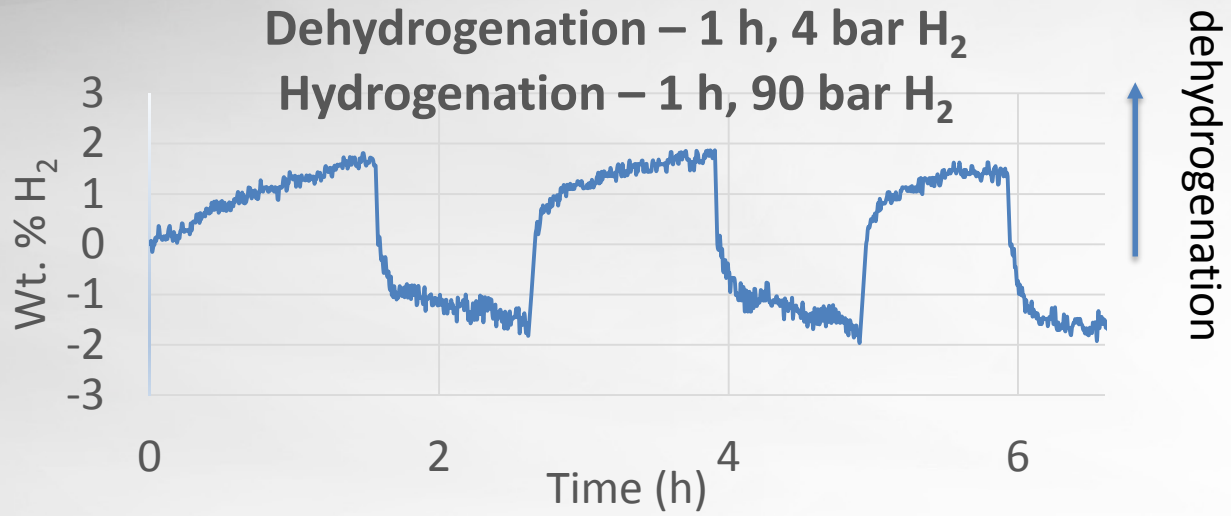


Highlight - systematic effort to understand the limitations to cycling $Mg(BH_4)_2 \Leftrightarrow MgB_{10}H_{10}$

Max H_2 density ca. 5.8wt% .25THF $Mg(BH_4)_2$

Craig Jensen

- **Thermodynamically feasible - but – how is it possible to reduce a closoborane, $MgB_{10}H_{10}$ to $Mg(BH_4)_2$ < 200 °C and < 100 bar H_2?**



- **PCT cycling (Hawaii)**
- **TPD/MS and DSC (NREL)**
- **Synchrotron XR (Norway)**
- **NVS (NIST)**
- **In-situ NMR, XRD, IR, RAMAN, calc *ΔG* (PNNL)**
- **Solvent free (Geneva)**

- **Thermodynamics favor regen of $Mg(BH_4)_2$ from $MgB_{10}H_{10}$ (ΔH ca. 38 kJ/mol)**
- **Additives, e.g., THF lower the mp of $Mg(BH_4)_2$.**
- **Sub-stoichiometric amounts, e.g., <1 THF/Mg results in a mixture of phases.**
- **Mixture melts between 70 – 100 °C to yield common amorphous phase.**
- **The melt amorphous phase is stable until ~ 180 °C, when H_2 is released to form $B_{10}H_{10}$ as the major product.**
- **Cycling limitations, heating too long or cooling to room temperature stops ability to cycle.**

Hydrogen carriers – task 3 work structure

Task 3 Carriers

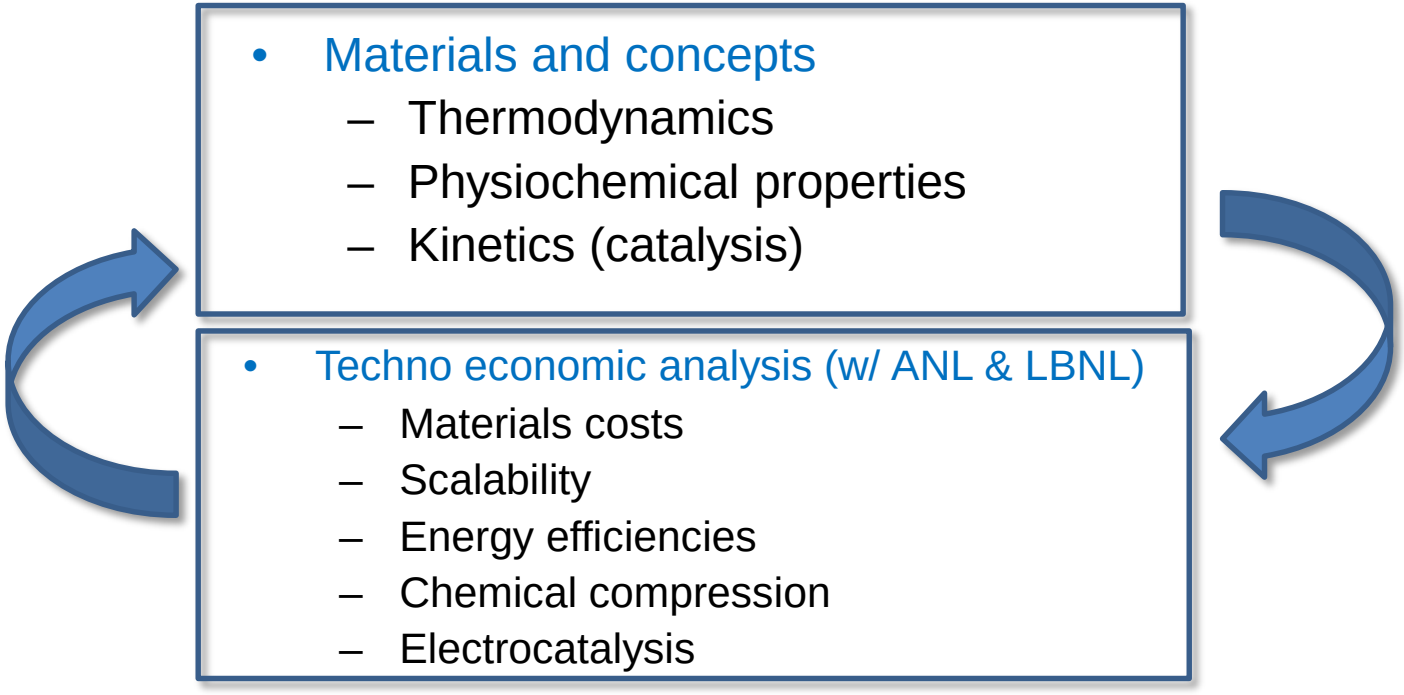
- 3.A Electrochemical approaches to produce hydrogen carriers (Wiedner)
  - Formation of H_2CO_2 from electrons, CO_2 and water
    - Current SOA; Dioxide Materials and O-CO
    - Future work – address the selectivity's, electrode material, HCO_2- or H_2CO_2
- 3.B.1 Dehydrogenative coupling (Nune)
  - no go
- 3.B.2 Aqueous organic carriers (PNNL, DICP)
  - Accomplishments: Kristons thermodynamic analysis for H_2 efficiency as function of ΔH and desired H_2 pressure (Chemical compression)
- 3.B.3 Formate/Bicarbonate cycle (PNNL, KIST) Grubel
  - Accomplishments: Karstens analysis
  - Progress: Show physiochemical properties
  - Future work: electrochemical cycle FS/BCS – what are the possibilities?
- 3.C.1 Magnesium borohydride melts (PNNL, NREL Hawaii, Geneva) Autrey
  - Ionic borohydrides (NREL)
  - Solvated contact ion pairs
  - Concept and future work need solvated ion pairs to enhance MH formation,

Dynamic connection between materials research and TEA

Accomplishments – PNNL and ANL webinar Dec 7th 2018

https://www.energy.gov/eere/fuelcells/downloads/hydrogen-carriers-bulk-storage-and-transport-hydrogen-webinar

February 17th brainstorming meeting on H_2 Carriers (PNNL, LBNL, NREL, SNL)



Take home: Hymarc will use TEA to help DOE identify material targets for H_2 carriers applications

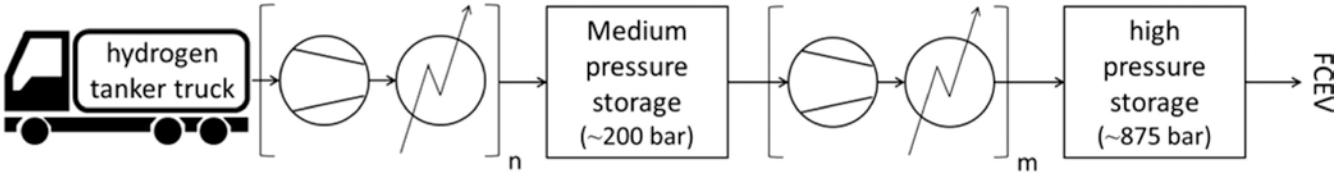
Concepts Chemical compression from formic acid

Max storage density ca. (FA) 53 g H_2/liter; generate >700 bar pressure

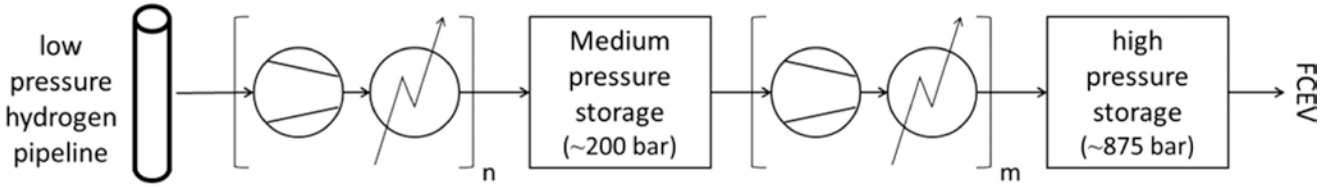
Karsten Mueller

- Top challenges
  - Separation of H_2 from CO_2 at high pressure
  - Preparation of H_2CO_2 by electrochemical processes

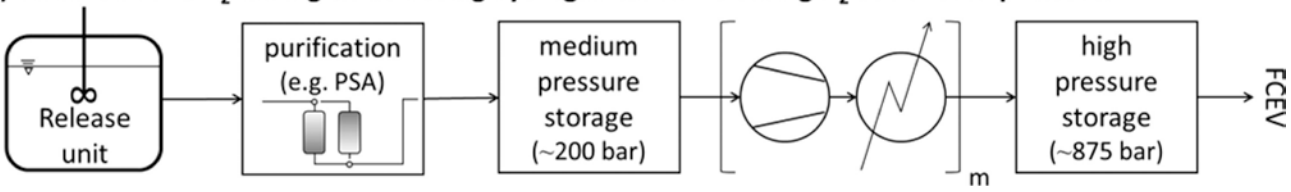
a) Schematic of a H_2 fueling station provided via trucks with pressurized hydrogen



b) Schematic of a H_2 fueling station based on a low pressure hydrogen source



c) Schematic of a H_2 fueling station using hydrogen carrier releasing H_2 at elevated pressures



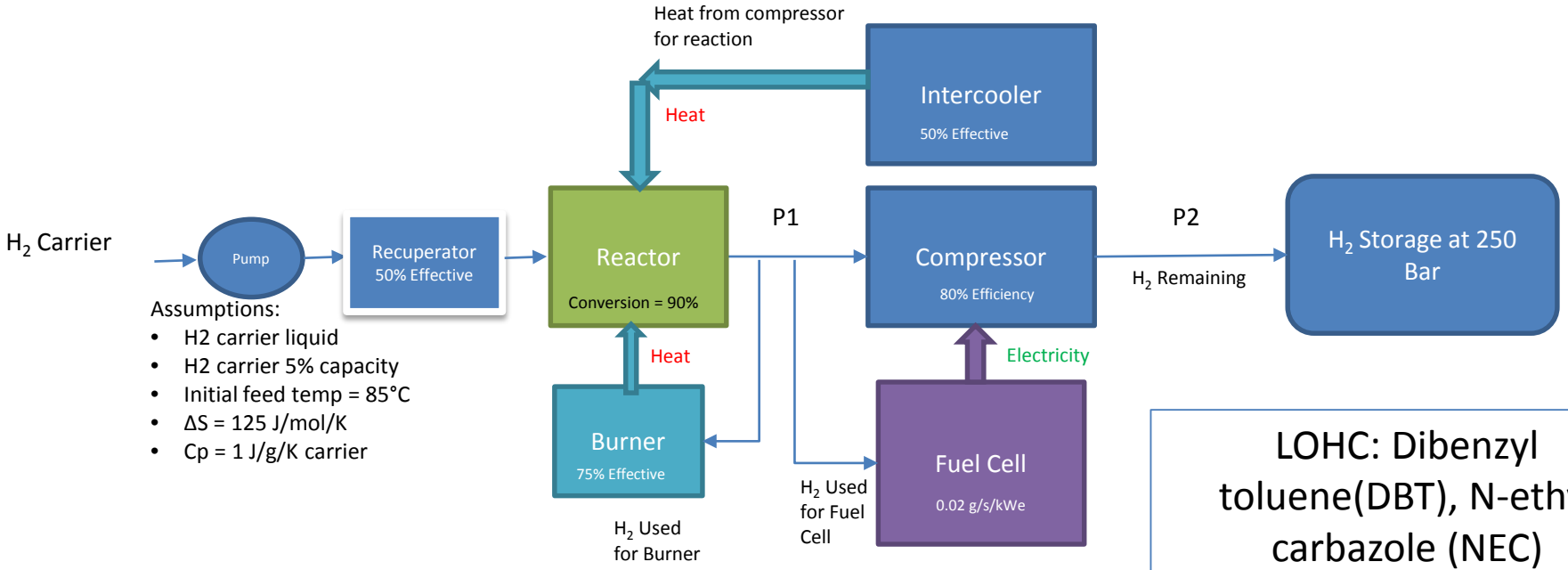
Releasing Hydrogen at High Pressures from Liquid Carriers: Aspects for the H_2 Delivery to Fueling Stations. Energy & Fuels. DOI:10.1021/acs.energyfuels.8b01724

Carriers. 3.B.2 Aqueous organic carriers

Take home: Modeling will help to identify the optimum balance between chemical and physical compression

Kriston Brooks

- How critical is a low ΔH – if you can burn H_2 from a higher density carrier to reach a greater overall efficiency?



- Distribution between pressure generation at reactor (chemical compression) and at compressor (physical compression)
- Calculate Efficiency for a range of ΔH (30-65 kJ/mol H_2) and pressures (1 - 250 bar)

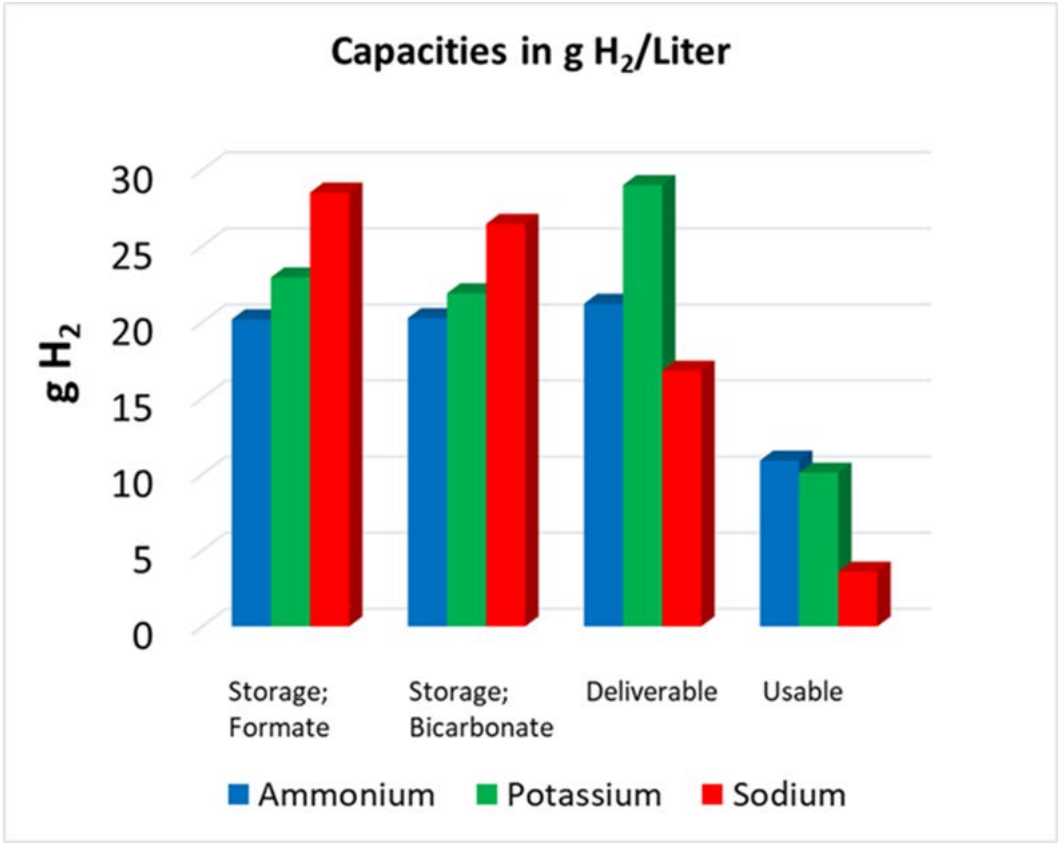
LOHC: Dibenzyl toluene(DBT), N-ethyl carbazole (NEC)
Max storage density ca.
(DBT) 56 g H_2/liter
(NEC) 53 g H_2/liter

Task 3 Carrier *Formate/Bicarbonate cycle (PNNL, KIST)*

- Water provides ½ the H_2

Hyangsoo Jeong

$$NaHCO_2 + H_2O \Leftrightarrow NaHCO_3 + H_2 \qquad \Delta G \sim 0$$



- *Storage capacity* – stored as a solid salt – add water later*
- *Deliverable capacity* - limited by solubility of formate
- *Usable capacity* – limited by solubility of bicarbonate

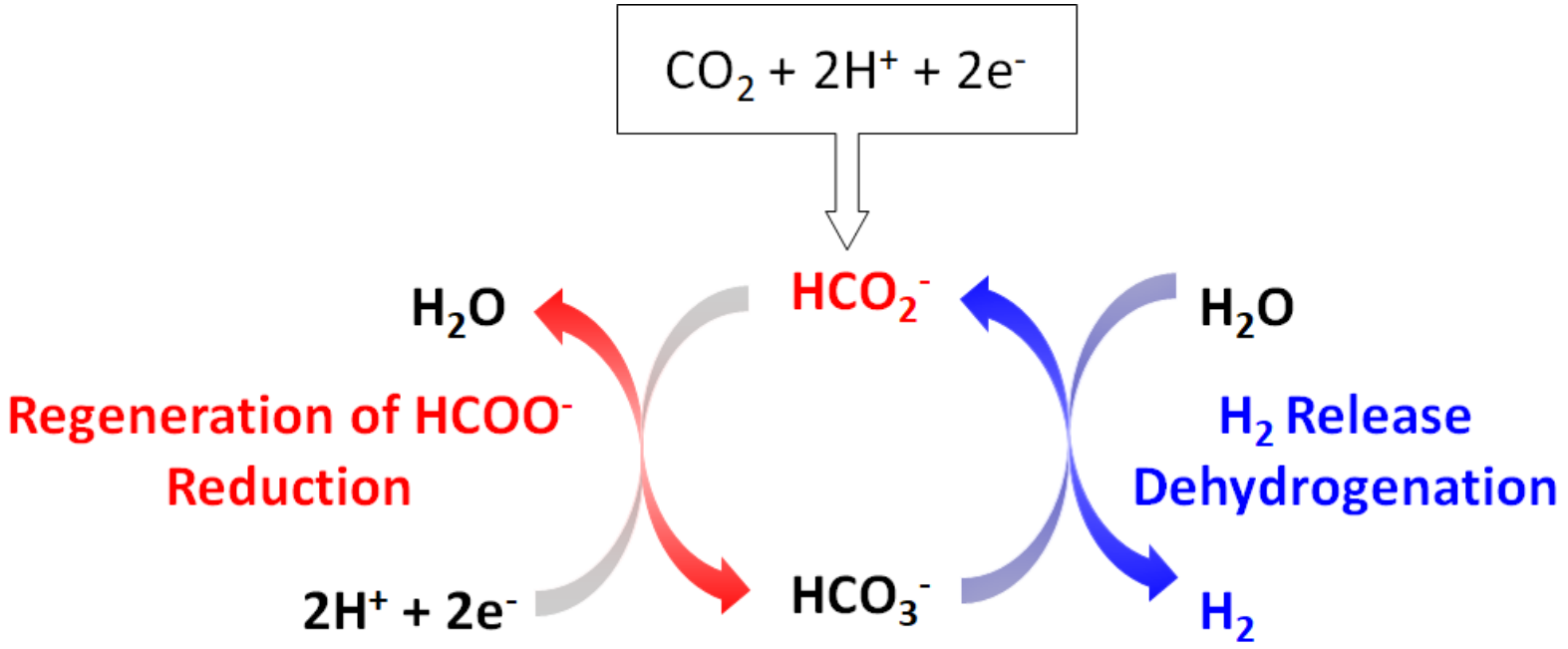
- *Is a formate salt a potential approach to store H_2 seasonally – "56 g H_2/liter"

Future work: concept of H_2 generation continuously

3.B.3 Formate/Bicarbonate cycle

Kat Grubel

- Concept: generate HCO_2- in a *first fill* then use electrocatalysis to regenerate formate from bicarbonate
- How do we optimize catalysis for H_2 release?



Formate H_2 carrier – continuously generate H_2 from electrons and water

Task 4. Capability Development: Sorbent, Hydrides and Hydrogen Carrier Characterization

- Develop and provide access to capabilities to
  - support seedling projects
  - measure properties to enable TEA
  - materials development
- Approach: experimental techniques to measure thermodynamics, rates, capacity, purity, physiochemical properties (pH, solubility)
  - High pressure reactors (Parr reactors, NMR, to measure hydrogen uptake and chemical compression
  - High pressure NMR
  - Gas burette equipped with pH meter, thermocouples with values for microGC, gas phase IR and flow meter, to measure kinetics, gas purity and pH).
  - benchtop NMR and react IR probe to follow evolution of chemical intermediates
  - Combi-catalysis reactors for catalysis studies

Mandatory summary slide

- Task 1. Sorbents
  - Developing solid state ^2H NMR capability 150 K and 100 bar H_2 pressure to provide a complimentary experimental approach to measure binding energies.
  - Model Pake pattern to obtain insight into dynamics – related to *ΔS & ΔH*
  - Investigating potential of heterolytic sorption of hydrogen (Lewis pairs)
- Task 2. Complex Hydrides
  - $THF_x(Mg(BH_4)_2$ (X<1) melts ~70 °C and remains amorphous may act as a 'catalyst' to stabilize and transfer BH_3*THF intermediates
  - Observe cycling so long as it remains liquid (working on how to maintain liquid phase)
  - Developing NMR experimental protocol for identifying borane intermediates
- Task 3. Hydrogen carriers
  - Looking at novel concepts and materials. (provide insight to develop targets)
  - DOE carriers webinar December 2018
  - Hymarc brainstorming February 2019 (defining metrics)

Remaining Challenges and Barriers

- An approach to maintain liquid phase of complex hydrides throughout the H_2 release (and uptake) cycle
  - Prevent phase separation of less soluble species
  - Understanding how the environment controlling reaction pathways (contact ion pairs)
- Light weight additives to control reaction pathways in complex hydrides
  - make $B_{10}H_{10}^{-}$
  - make $B_3H_6^{2-}$ to avoid phase separation of MgH2
- Optimizing balance between physical and chemical compression LOHCs
- Novel approaches to tune thermodynamics of hydrogen carriers to lower 'operating' temperature to release H_2 from hydrogen carriers
- Synthesis of hydrogen carriers without using H_2

Future work

Collaborations to optimize properties of LOHC for hydrogen carriers

KIST (Korea) Chang Won Yoon and Hyangsoo Jeong. Catalysts for H_2 release from formate salts.

AIST (Japan) Qiang Xu, Yuichi Himeda and Hajima Kawanami Catalysts for H_2 release from formic acid (MOU)

DICP (Hydrogen storage, conversion and utilization (Jan. 2019 to Dec. 2021) lead by Ping Chen and Teng He with PNNL, Tejs Vegge, Martin Dornheim.

Acknowledgements

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Publications

Pacific Northwest NATIONAL LABORATORY
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