SAND2019-3765PE

Melt-Infiltration of Magnesium Borohydride in Nanoporous Carbons for High-Density Hydrogen Storage

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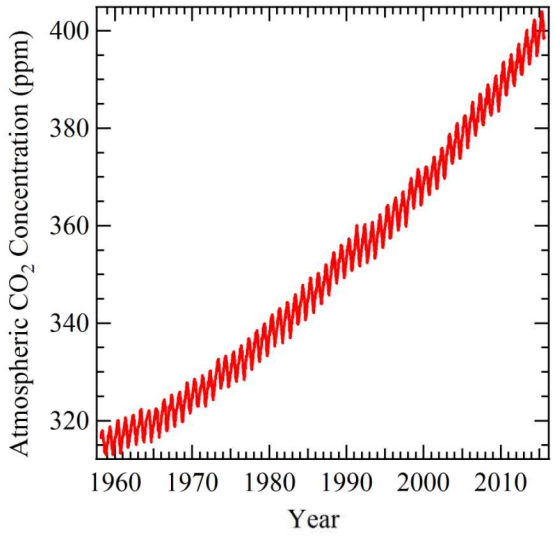
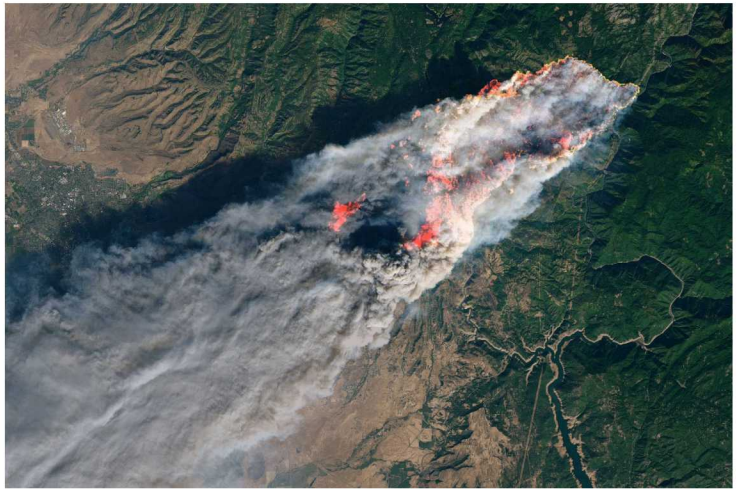
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Outline

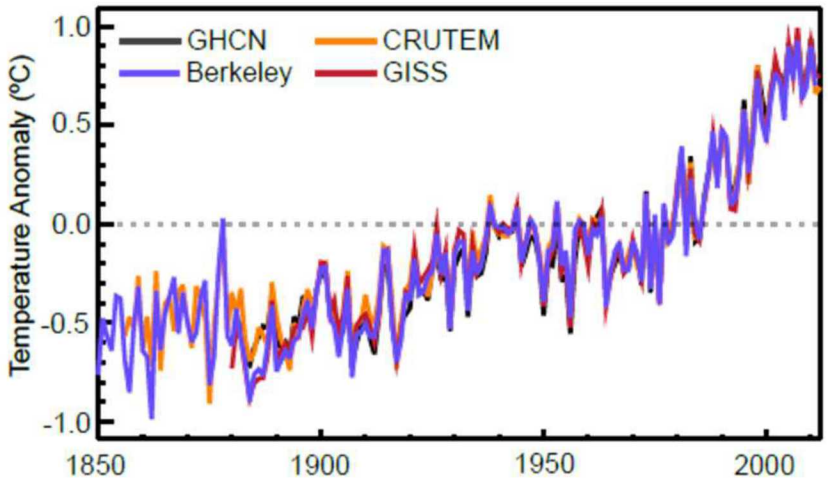
- Solid hydrogen storage: why is it important?
- Magnesium borohydride as high-capacity material
- Chemical stability and melting of $Mg(BH_4)_2$
- Formation and characterization of nanoscale $Mg(BH_4)_2$@C composites
- Conclusions
- Future work

Anthropogenic Climate Change

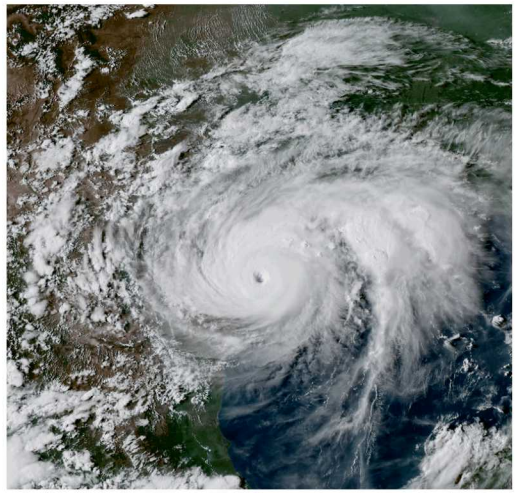




Camp Fire, 2018



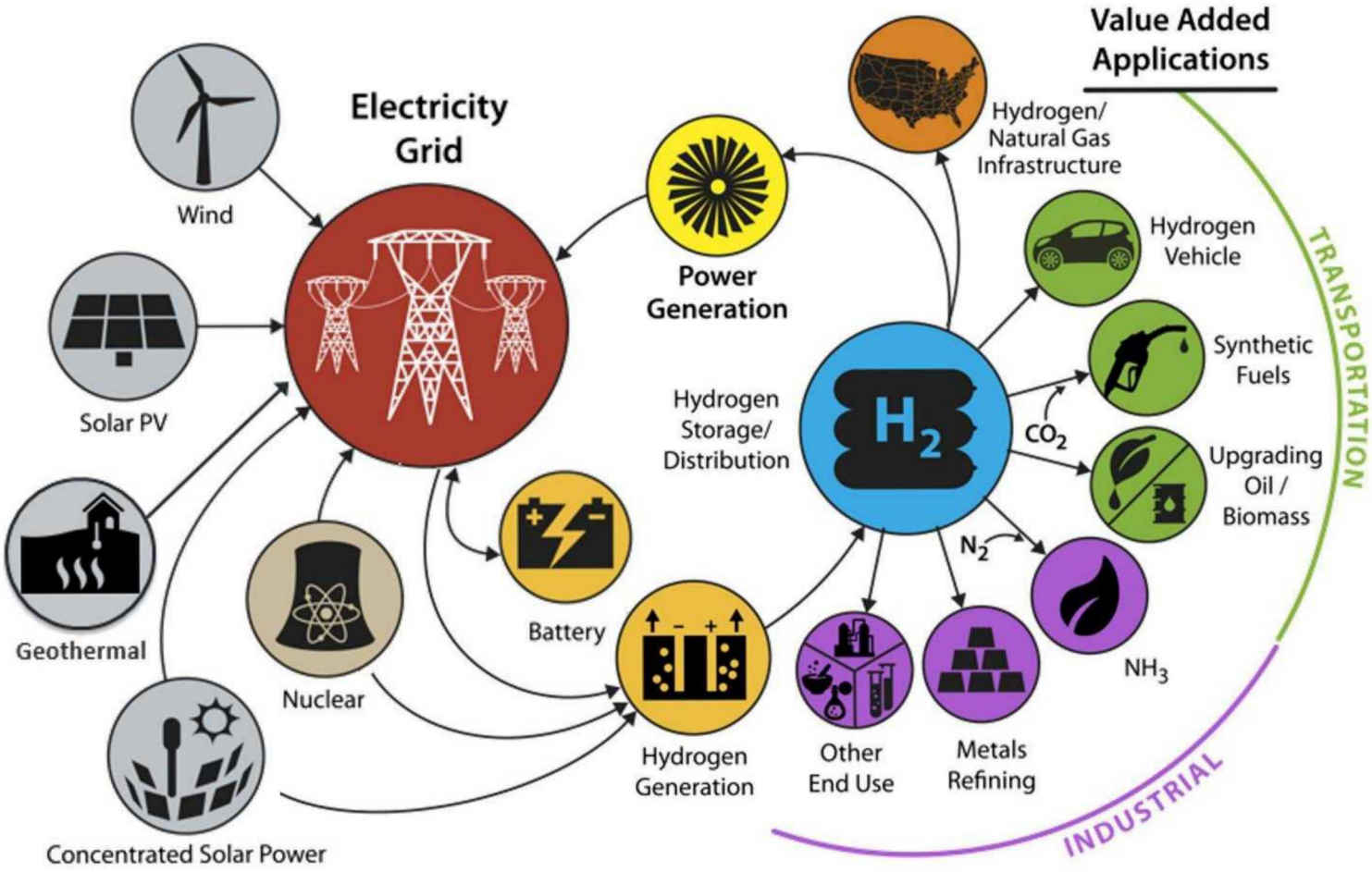
IPCC Fifth Assessment Report, 2013



Hurricane Harvey, 2017

Shift from Fossil to Renewable Energy

The Hydrogen Economy



Storage as Hydrogen

- High gravimetric energy density
  - 1 kg H_2 equivalent to 3 kg (1 gallon) gasoline
- Very low volumetric energy density
  - >3000 gallons H_2 (STP) equivalent to 1 gallon gasoline

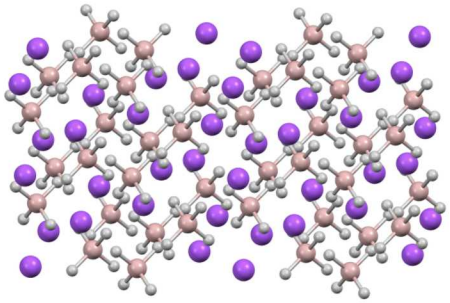
Compress

40 kg H_2 m^{-3} at 700 bar

Liquefy

70 kg H_2 m^{-3} at 21 K

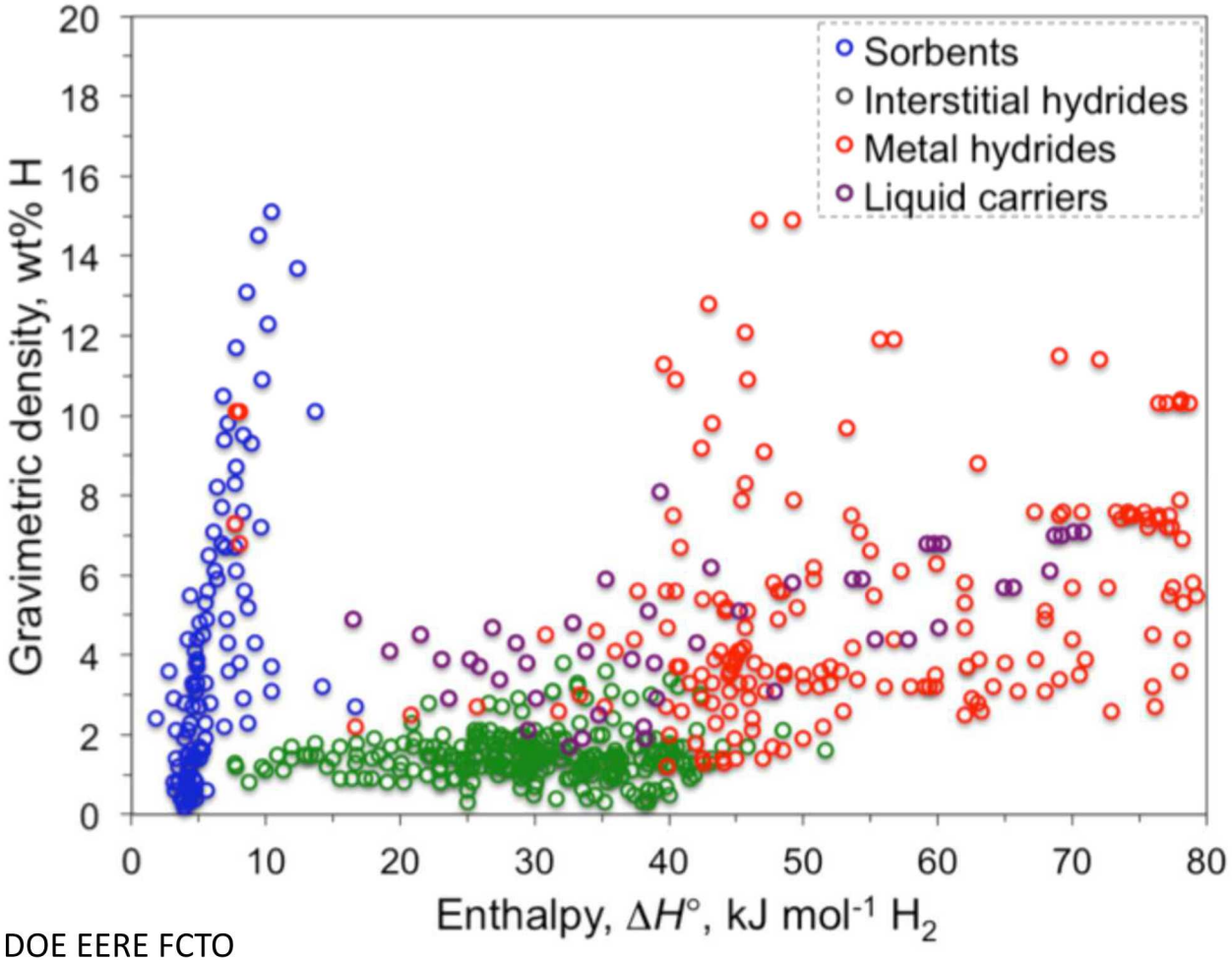
Solidify



Bloś et al., Science 365, 145 (2019)

> 100 kg H_2 m^{-3} at RT in metal hydrides

Vehicular Hydrogen Storage Goals



DOE EERE FCTO

- DOE 2020 System Targets
  - 5.5 wt% H_2
  - 40 g H_2 / L
  - 85° C max delivery temp. ($\Delta H \approx 20$-30 kJ/mol H_2)
  - Reversible (1500 cycles)
  - 1.5 kg H_2 / min fill rate

Need "Goldilocks" thermochemical properties and fast kinetics!

Sandia National Laboratories

Lawrence Livermore National Laboratory

BERKELEY LAB
Lawrence Berkeley National Laboratory

Goals

"Foundational understanding, synthetic protocols, new characterization tools, and validated computational models" for hydrogen storage materials to meet industry requirements for vehicles

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

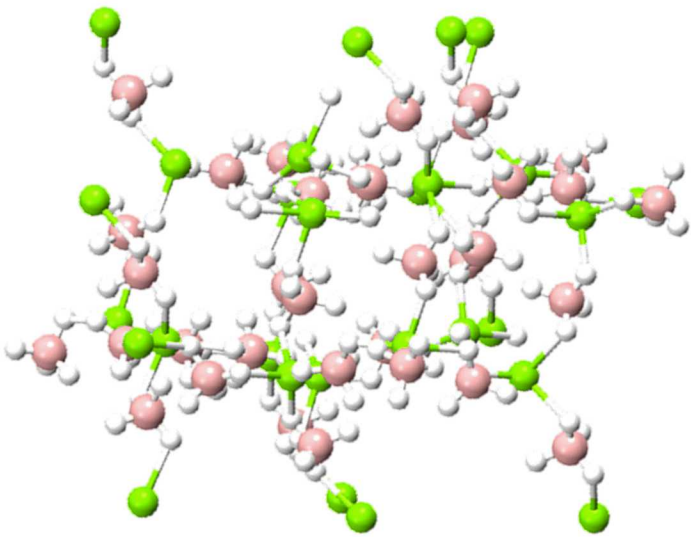
SLAC
NATIONAL ACCELERATOR LABORATORY

Pacific Northwest
NATIONAL LABORATORY

NIST
National Institute of Standards and Technology

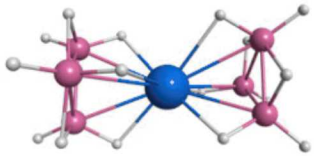
Magnesium Borohydride

- One of the highest capacity light complex metal hydrides
- Multiple low-temperature (α,γ) and one high-temperature (β) phases
- 14.9 wt.% H gravimetric capacity
- 113 g H_2/L volumetric density (β-phase)



BH_4^- tetrahedral complex ions coordinating Mg^{2+} ions

$Mg(BH_4)_2$



-2.5 wt.% H

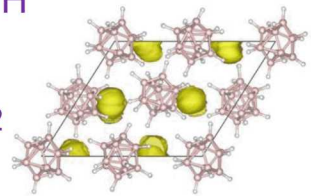
$Mg(B_3H_8)_2$

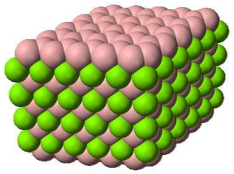
-8.1 wt.% H

$MgB_{10}H_{10}$

-8.0 wt.% H

$MgB_{12}H_{12}$





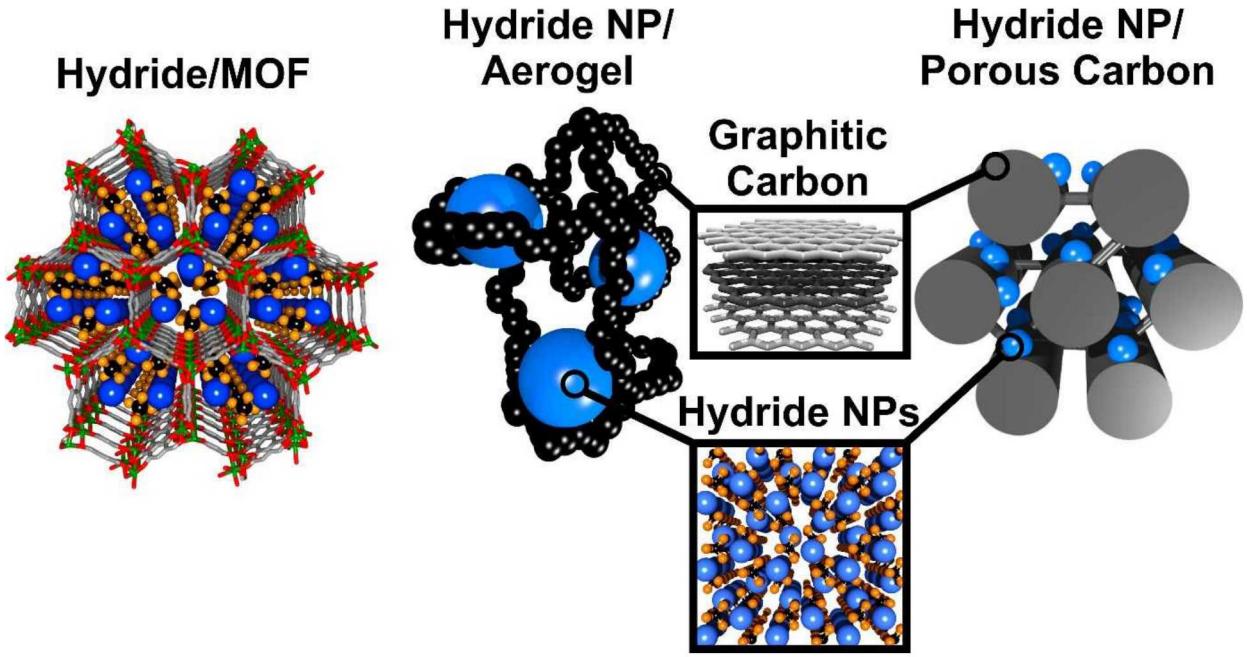
MgB_2

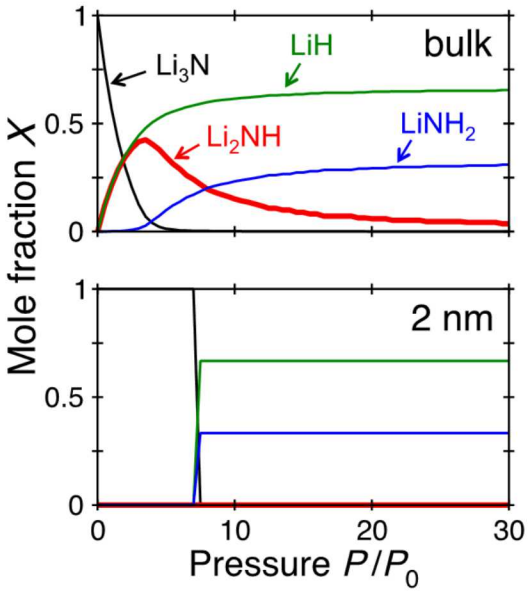
Very complex boron cluster chemistry

High temperature (~ 600 °C) needed for complete desorption

Reversibility only at high H_2 pressures (> 500 bar)

Nanoconfinement





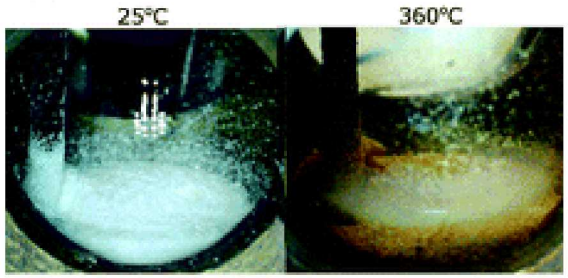
Nanoconfined Li_3N has no Li_2NH intermediate, avoids kinetic trap

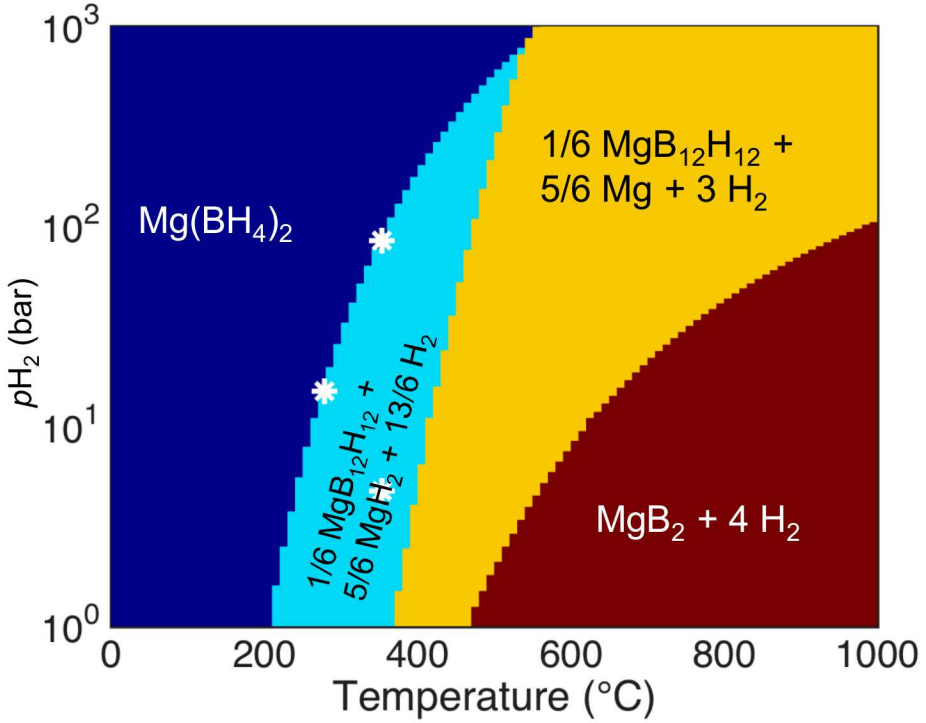
- Constrict hydride to nanoscale
- Improve thermodynamics
- Enhance kinetics
- Reduce intermediate formation

Chem. Rev. **2018**, *118*, 10775−10839
Adv. Mater. Interfaces **2017**, *4*, 1600803

Thermodynamics of $Mg(BH_4)_2$

- Calculated phase diagram: No $Mg(BH_4)_2$ melting as claimed by several reports
- Fast temperature ramps for melting fail to outpace decomposition



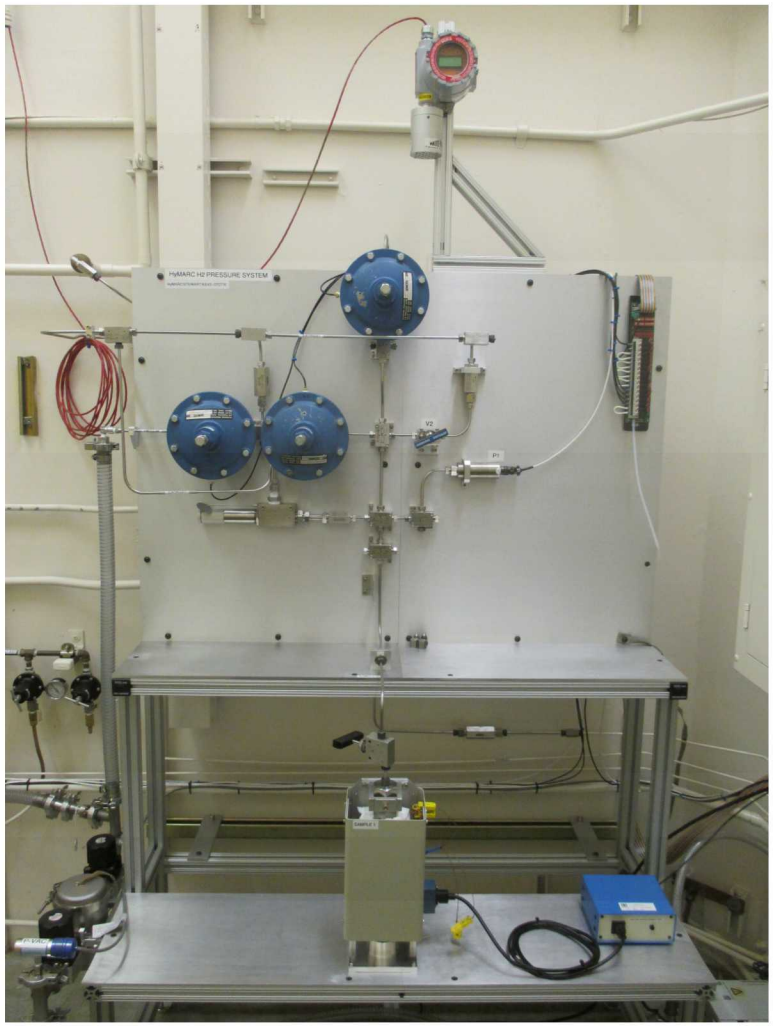


Computed Mg-B-H phase diagram (LLNL)

Need stable determination of melting point!

J. Phys. Chem. C **2012**, *116*, 15231
Phys. Chem. Chem. Phys. **2013**, *15*, 19774

Utilizing High H_2 Backpressure



Custom high-pressure hydrogen system (B976)
0-1000 bar, 25-400 °C

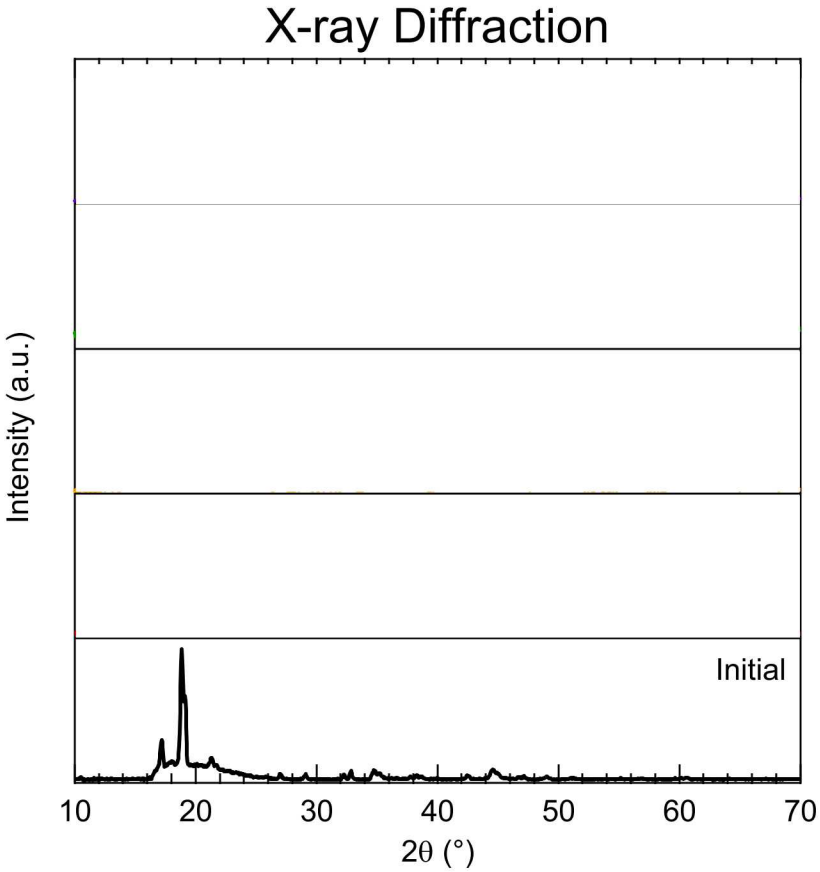
Load up to 4 samples in vessel inside glovebox

Pressure-Dependent Stability

Heated β-$Mg(BH_4)_2$ samples up to 400 °C

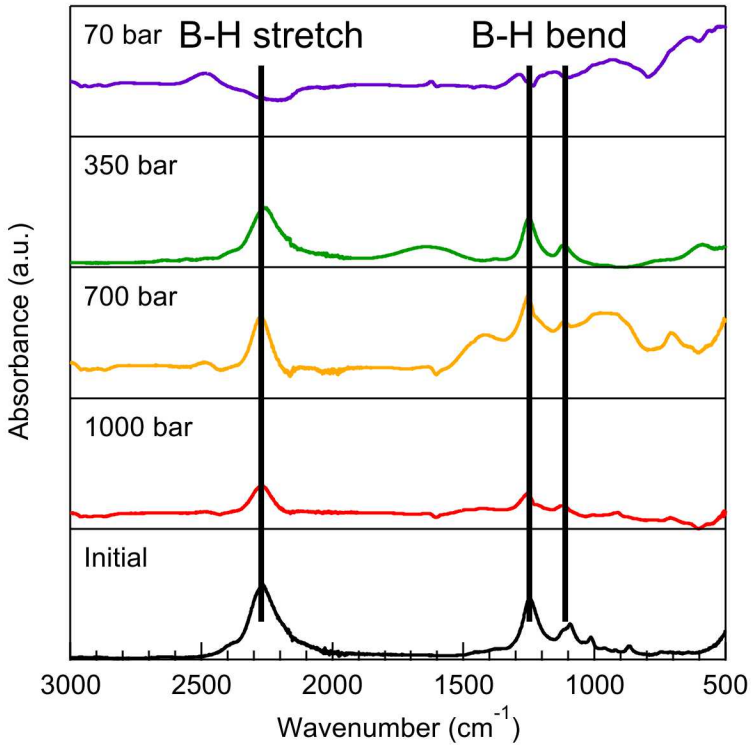
Melting (and resolidification) observed at highest pressures

Amorphization and decomposition below 700 bar



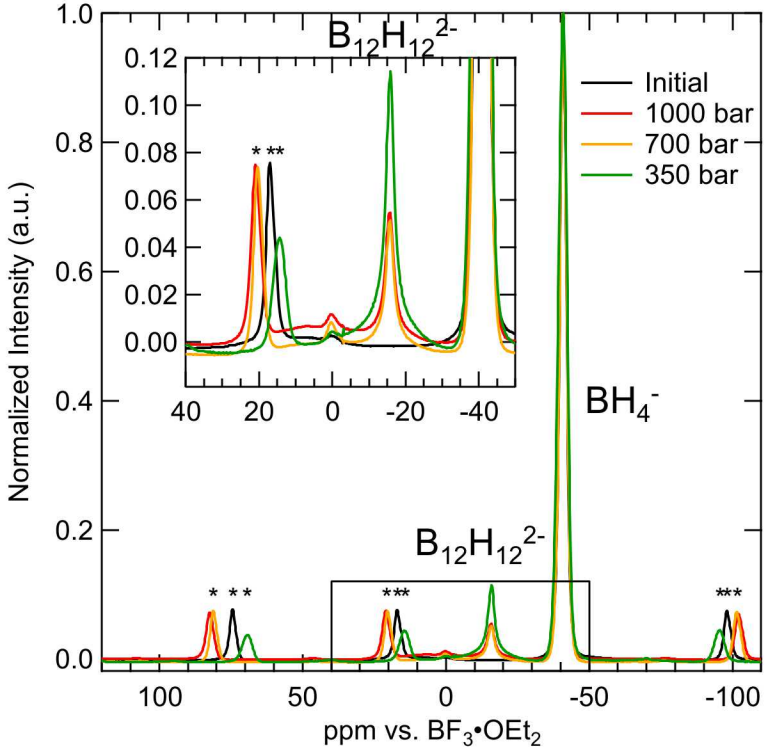
Further characterization

FTIR



B-H IR peaks only disappear below 350 bar

Solid-State ^{11}B NMR



$B_{12}H_{12}^{2-}$ formation observed

→ *$Mg(BH_4)_2$ is stable only under very high H_2 backpressures*

* spinning side bands

Melting Point Determination

Pressurized $Mg(BH_4)_2$ to 1000 bar and heated, then cooled

340 °C (powder, not shown)

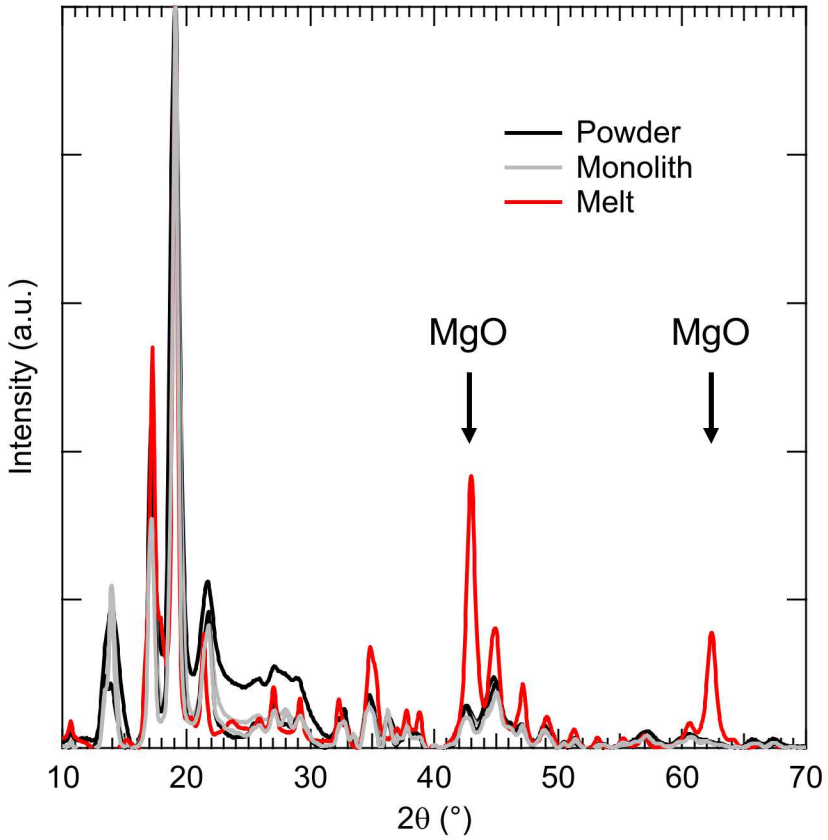
Thermal gradient

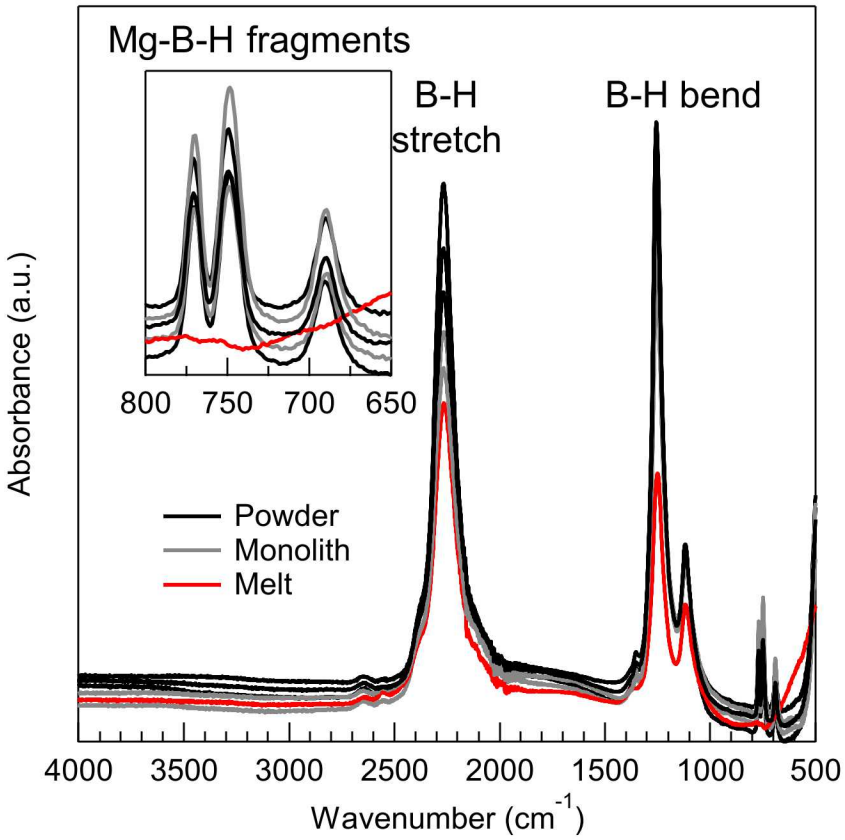
357 °C, top (compacted monolith)

top (melt) mid (monolith) 367 °C bottom (powder)

→ *$Mg(BH_4)_2$ melting point is ~370 °C, 90 °C higher than previously reported*

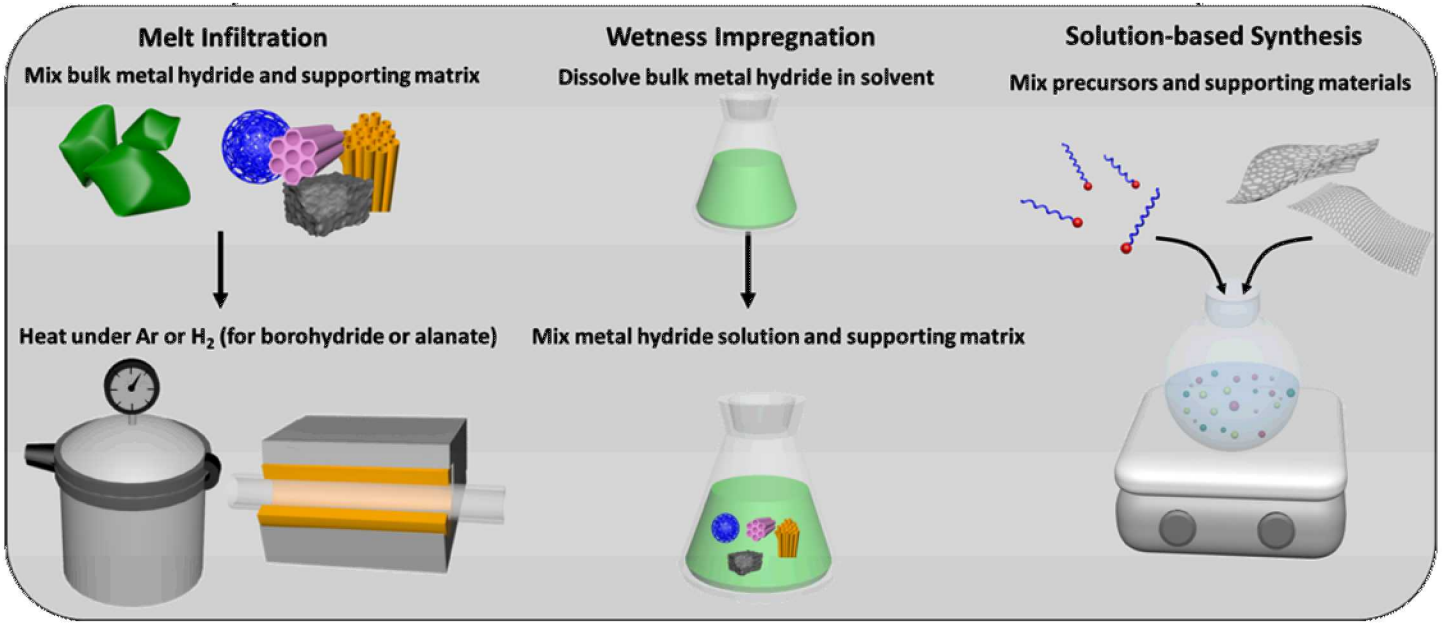
Heated Sample Characterization





→ MgO XRD peaks and loss of Mg-B-H fragment
IR peaks indicate partial oxidation upon melting

Application of Melting to Nanoconfinement

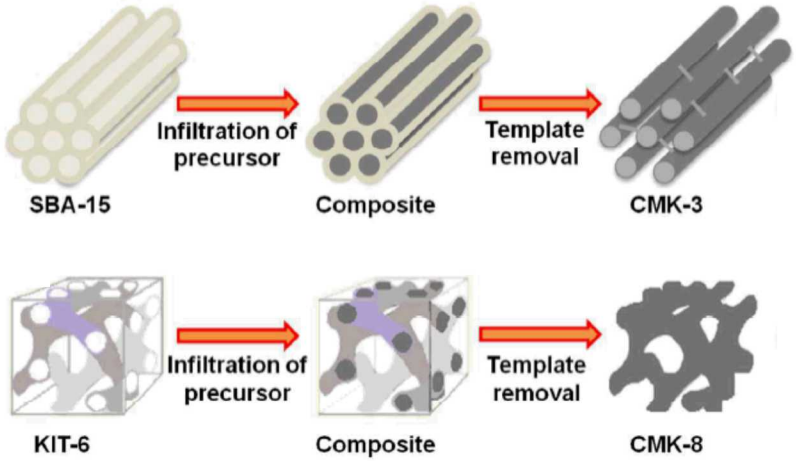


Methods with solvents limit loading, introduce contaminants that are hard to remove

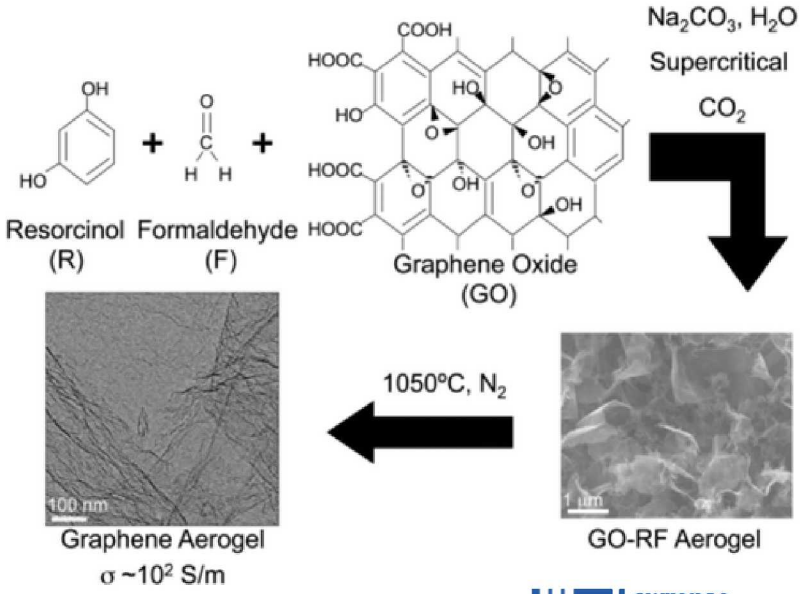
Melt infiltration of hydride into nanoporous host occurs by capillary action

Porous Carbon Hosts

Ordered Mesoporous Carbons



Graphene Aerogels

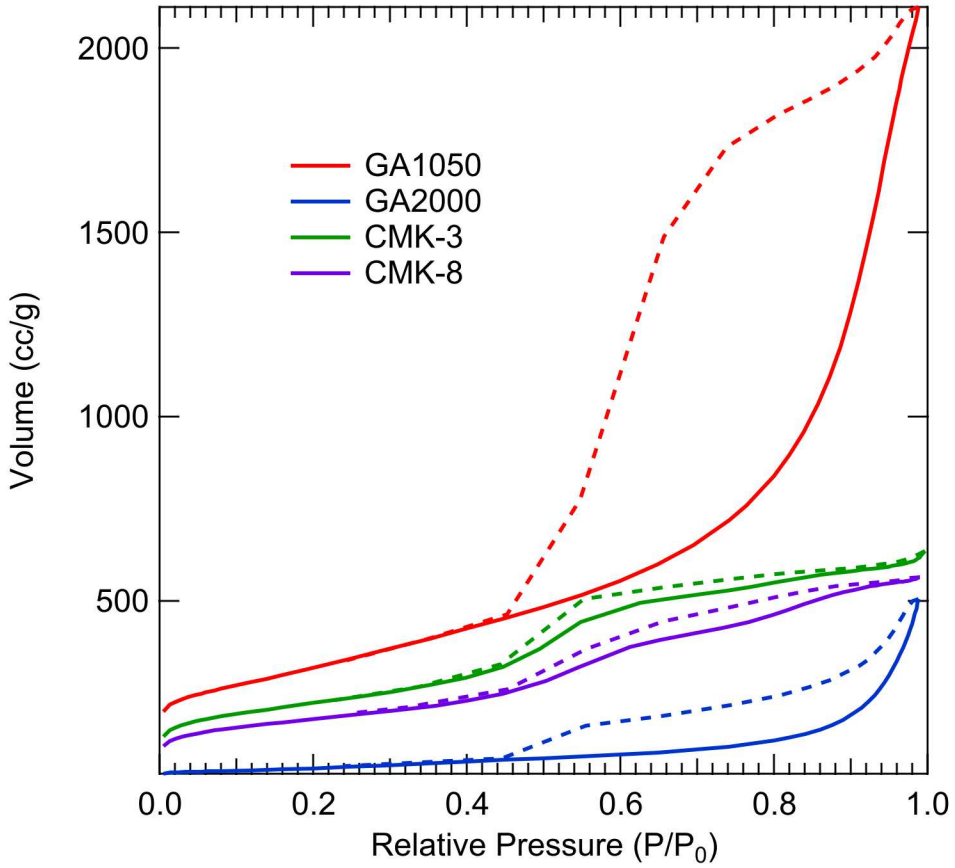


From collaborators at Lawrence Livermore National Laboratory

Carbon N_2 Adsorption Porosimetry

Carbon	BET Area (m^2/g)	Pore Volume (cc/g)	Avg. Pore Radius (nm)
GA1050	1112	3.25	5.5
GA2000	155	0.77	9.0
CMK-3	782	0.96	2.5
CMK-8	629	0.87	2.8

Chosen carbons have large pore volumes for holding hydride: minimize inactive dead weight



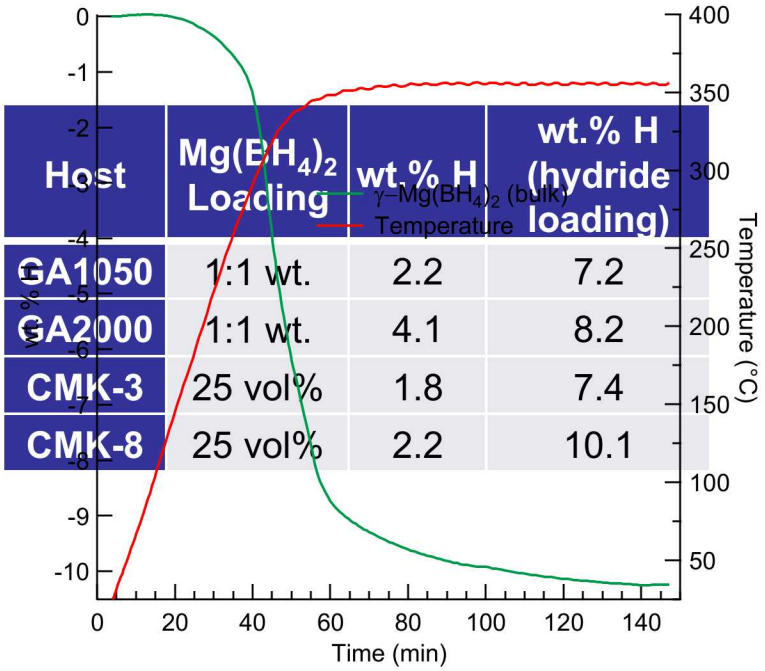
Melt Infiltration

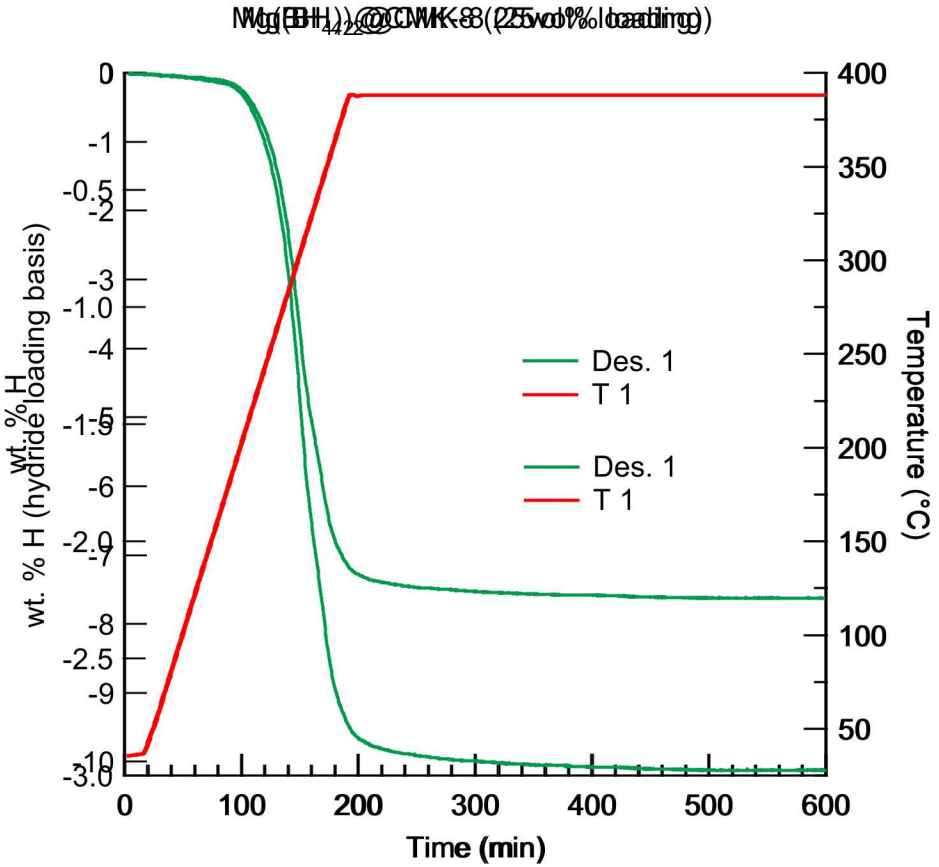
- Physically mix $Mg(BH_4)_2$ and carbon
  - Aim for ratios based on carbon's total pore volume or total mass
- Melt at 400 °C with 1000 bar H_2 backpressure for 16 h
- Grayish initial mixture yields black composite powder after infiltration, indicating absorption of $Mg(BH_4)_2$

Hydrogen Storage of Composites

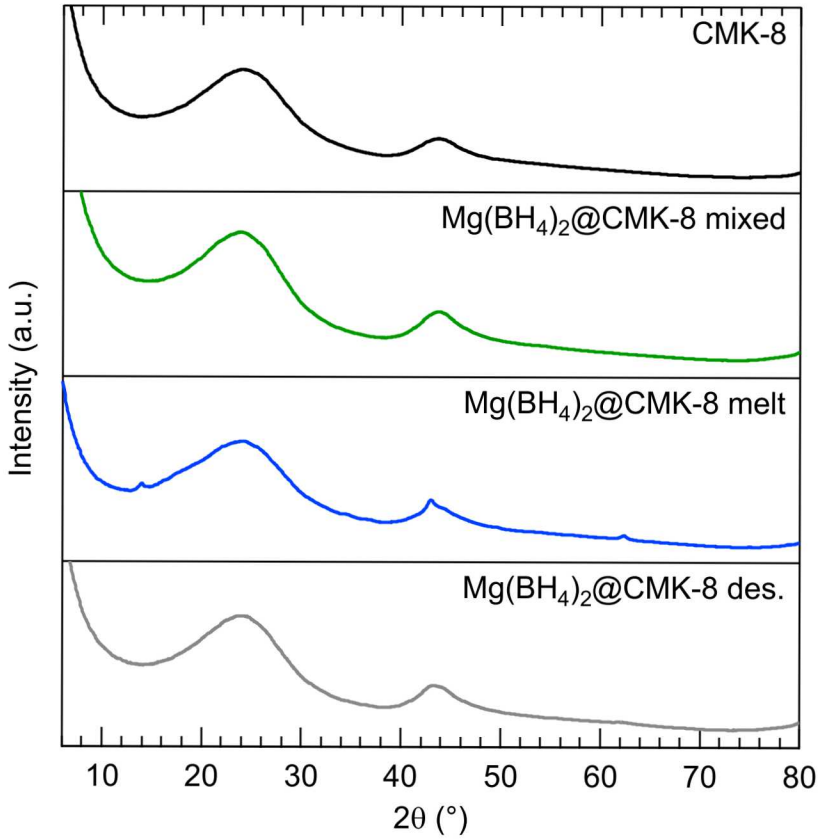
- Heat sample in Sieverts apparatus
- Measure change in gas pressure
- Convert P to wt.% H given known volumes and sample mass

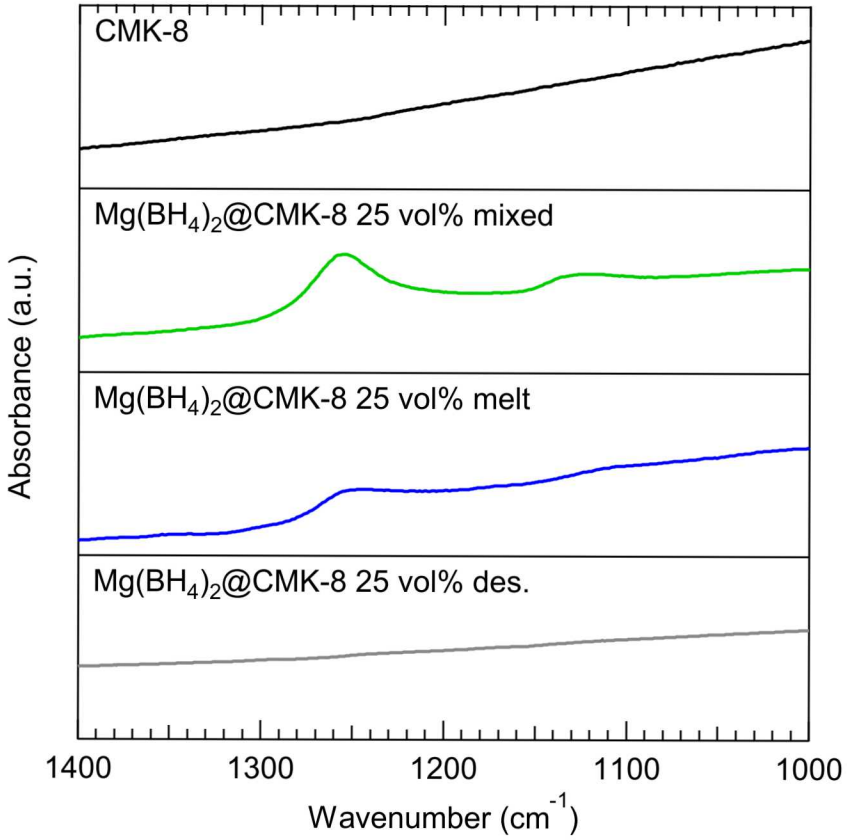
Host	$Mg(BH_4)_2$ Loading	wt.% H	wt.% H (hydride loading)
GA1050	1:1 wt.	2.2	7.2
GA2000	1:1 wt.	4.1	8.2
CMK-3	25 vol%	1.8	7.4
CMK-8	25 vol%	2.2	10.1





Composite Characterization

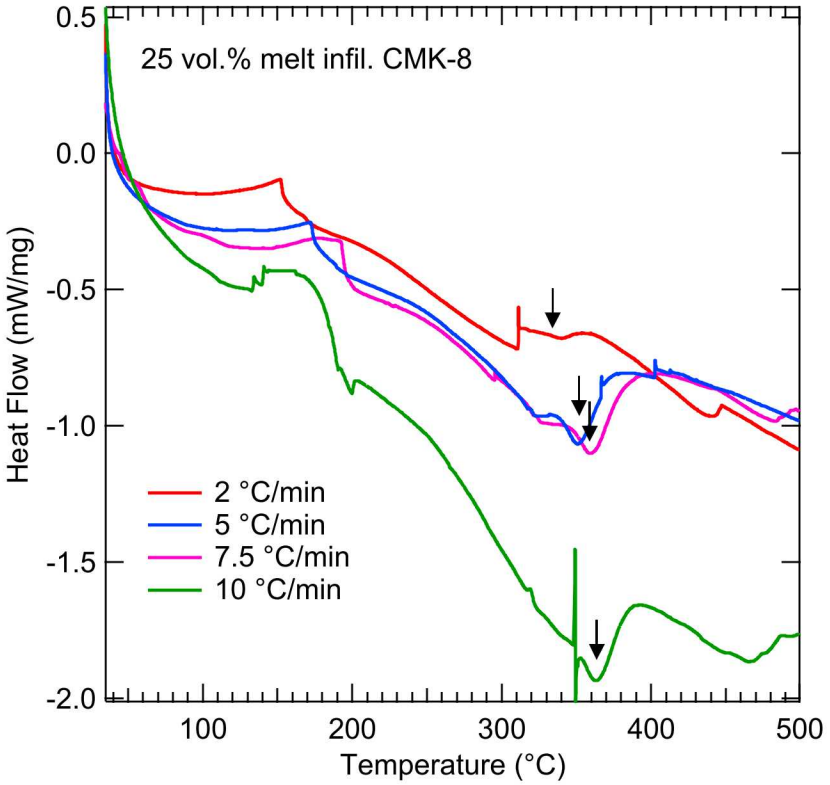


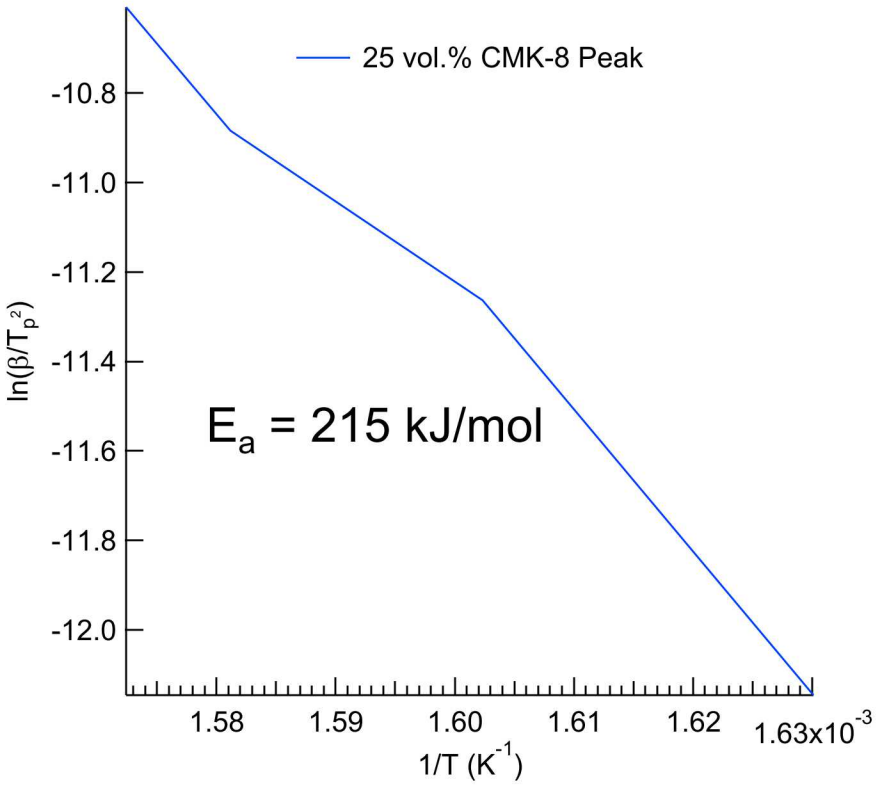


Kinetic Analysis: Kissinger Method

Use differential scanning calorimetry (DSC) to get reaction rates

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{R}\left(\frac{1}{T_m}\right)$$

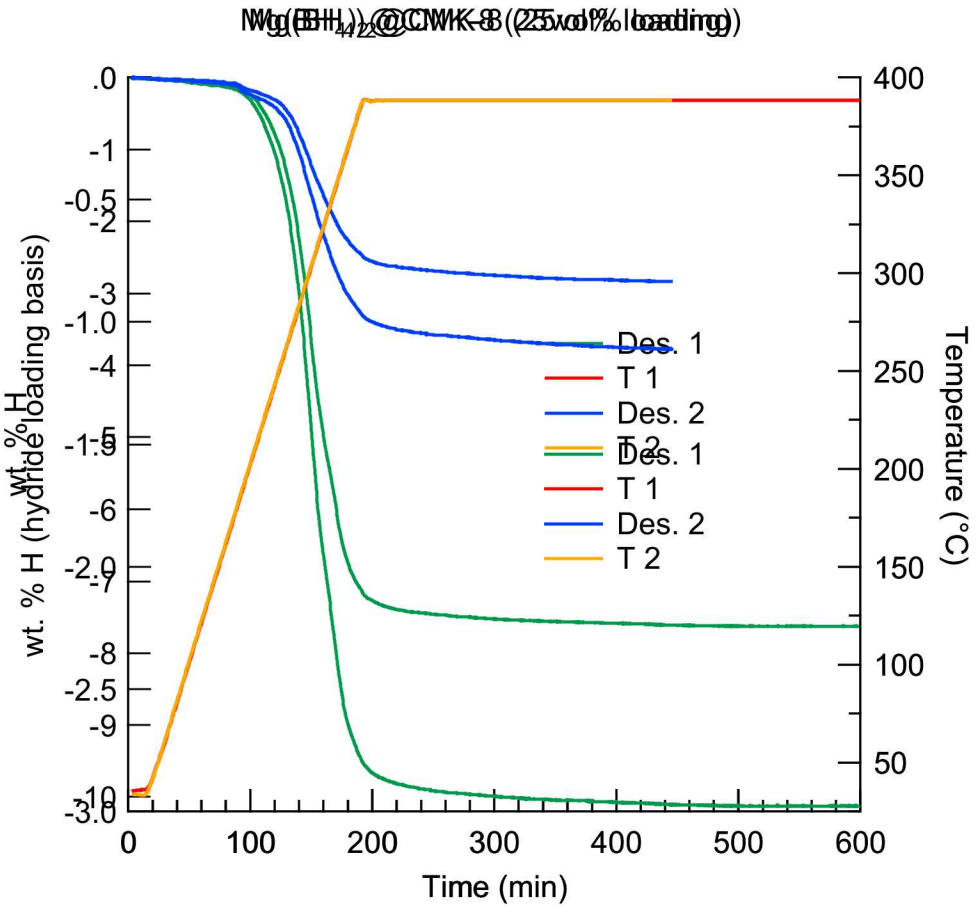




Rehydrogenation

Rehydrogenated by heating to 320 °C, 100 bar H_2, 20 h

Significant loss of H capacity

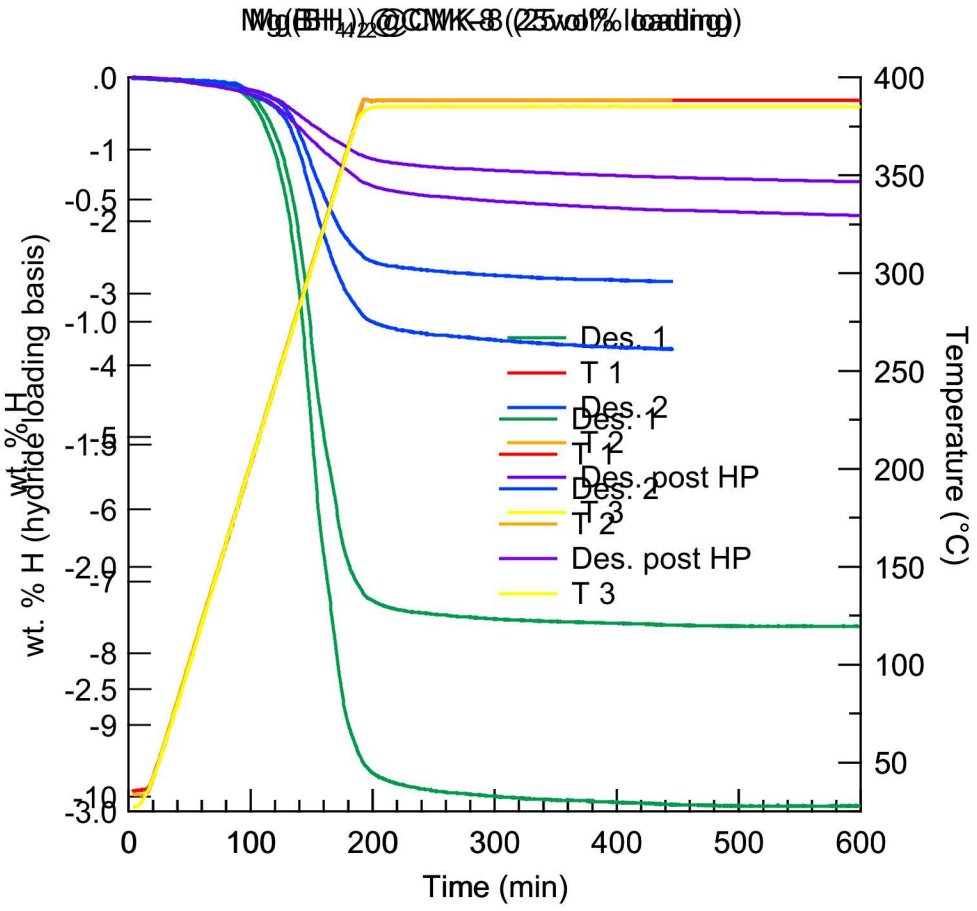


High-Pressure Rehydrogenation

Rehydrogenated by heating to 400 °C, 1000 bar H_2, 72 h

Capacity even lower after HP rehyd.

Host	wt.% H (hydride loading), 1st des.	wt.% H (hydride loading), 2nd des.	wt.% H (hydride loading), 3rd des.
GA1050	7.2	2.1	1.4
GA2000	8.2	4.1	0.8
CMK-3	7.4	3.1	1.6
CMK-8	10.1	3.8	1.9



Potential Issues

- Incomplete dehydrogenation
- Formation of meta-stable intermediates
- Cycling between Mg and MgH_2 rather than MgB_2 and $Mg(BH_4)_2$
- Reaction of Mg with carbon support

Conclusions

- High H_2 backpressures required for $Mg(BH_4)_2$ stability
- Significant decomposition at pressures as high as 350 bar H_2
- Melting of $Mg(BH_4)_2$ occurs at ~370 °C without significant decomposition
- Melt-infiltration into nanoporous carbons enabled
- H_2 capacity of composites similar to that of bulk $Mg(BH_4)_2$
- Incomplete desorption leads to poor cyclability and reversibility
- Thermodynamic and kinetic characterization of composites required

Future Work

- Increase loading (up to 100 vol%)
- NMR of composites before and after desorption and rehydrogenation
- Determine activation energies of various steps
- Ascertain ΔH and ΔS

Acknowledgments

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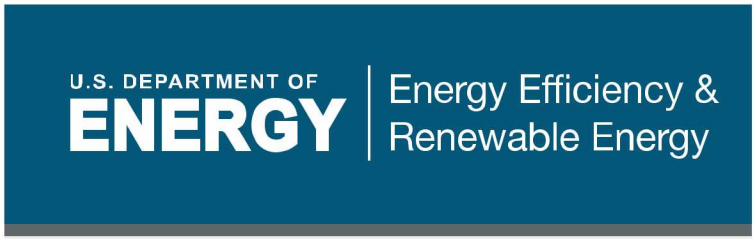

Ned Stetson, Program Manager
Jesse Adams
Zeric Hulvey

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