SAND2019-3177PE

# HyMARC: Addressing Key Challenges to Hydrogen Storage in Advanced Materials Through a Multi-Lab Collaboration

HyMARC
Hydrogen Materials Advanced Research Consortium

***Enabling twice the energy density for onboard $H_2$ storage***

**Mark D. Allendorf, Sandia National Laboratories**
**Tom Gennett, National Renewable Energy Laboratory**

NREL NATIONAL RENEWABLE ENERGY LABORATORY · Sandia National Laboratories · Lawrence Livermore National Laboratory · Berkeley Lab · Pacific Northwest National Laboratory · NIST · SLAC National Accelerator Laboratory





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**Project ID: ST127**

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# Overview

## Timeline

Phase 1: FY16 – FY18
Phase 2 FY19 – FY22

## 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 Chemisorption

O. Test Protocols and Evaluation Facilities

## Budget

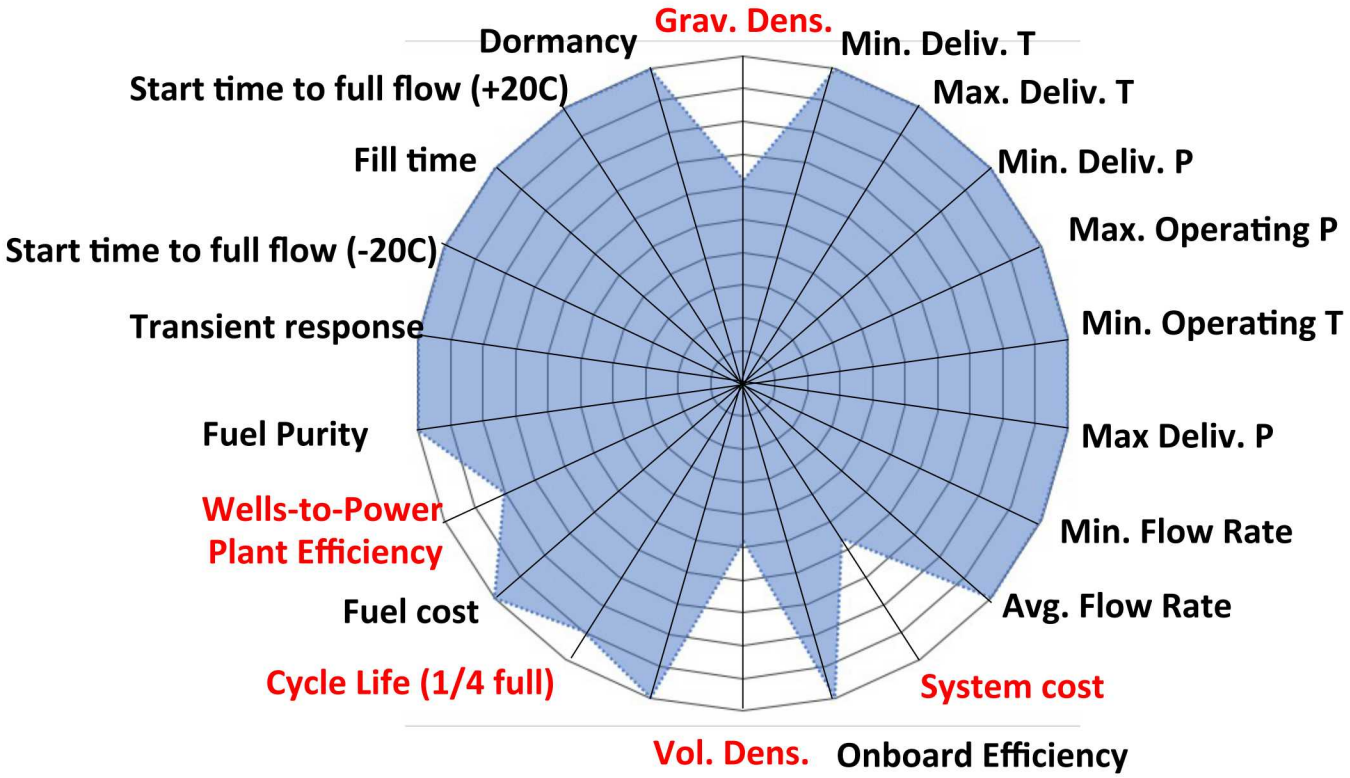
| | |
|---|---|
| FY18 Phase 1 Funds: | $3,820K |
| FY18 DOE Funding for Phase 2: | $5,501K |
| FY19 DOE Funding (as of 3/31/19): | $2,350K |
| Total DOE Phase 2 Funds Received: | $7,851K |

## Partners

- Sandia National Laboratories
- National Renewable Energy Laboratory
- Lawrence Livermore National Laboratory
- Lawrence Berkeley National Laboratory
- Pacific Northwest National Laboratory
- SLAC Accelerator Laboratory
- NIST Center for Neutron Research

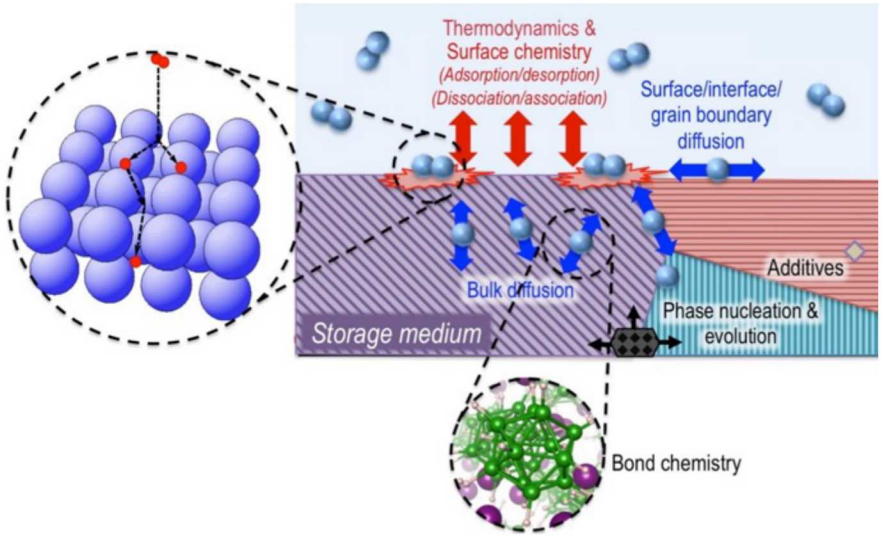
# Relevance: Although fuel cell vehicles are now commercially available, compressed $H_2$ storage falls short of several DOE targets

**700 Bar Compressed Gas (2015 record) vs. revised ultimate Targets**

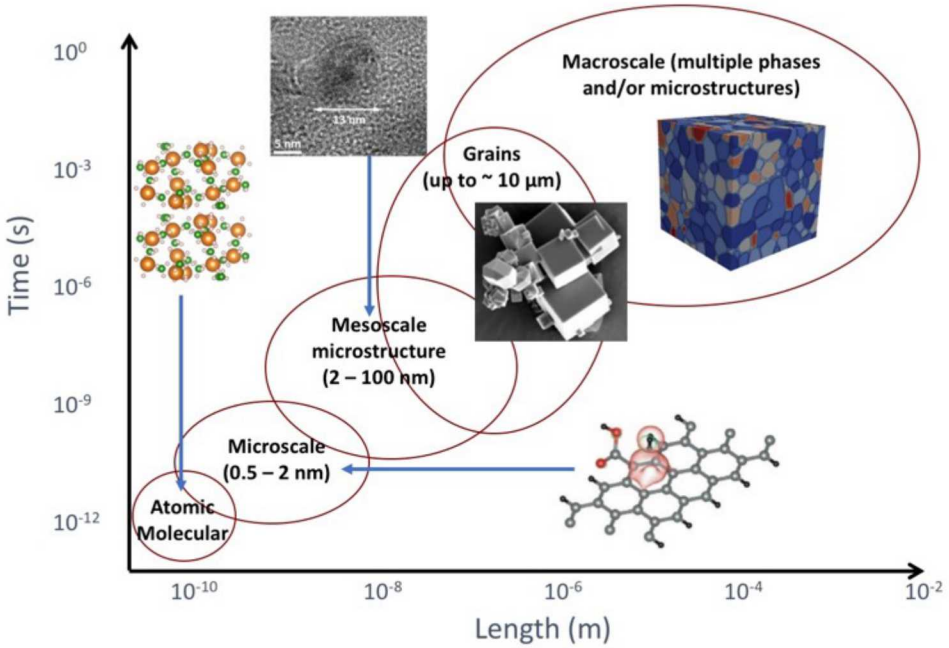


# Relevance: poorly understood phenomena at length scales from < 1 nm to μm govern storage material behavior

**Distinct chemical/physical processes affect the bulk properties of storage materials**




**Multiple length scales must be taken into account**




*"Design rules" are needed to guide materials discovery*

# Objective: HyMARC aims to accelerate materials discovery

***Assemble small, agile teams comprising synthetic, characterization, and modeling expertise***

**Foundational knowledge gaps**
- Model material systems
- Thermodynamic data
- Kinetic data
- Microstructural features

- **Structure-property relationships**
- **Rate-limiting steps**
- **What material features really matter?**

**New core capabilities**
- Computational models
- Characterization tools
- Novel material platforms

- **Probe and predict at all relevant length scales**
- **State-of-the-art tools for materials discovery**
- **Assist Seedling projects**

**Evaluate new material concepts**
- Assess potential
- Perform high-accuracy measurements

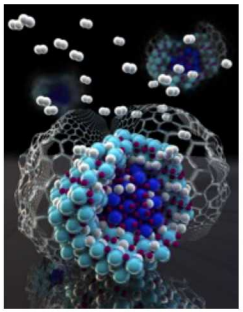
- **Define new research directions**
- **Provide guidance to DOE for funding investments**

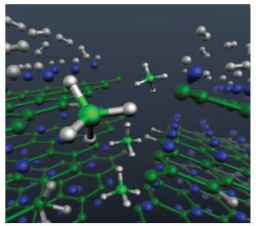
**"Gold standard" measurements**
- Variable T PCT
- Thermal conductivity
- Ultrahigh-pressure reactor

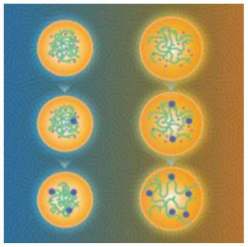
- **Validate claims, concepts, and theories**

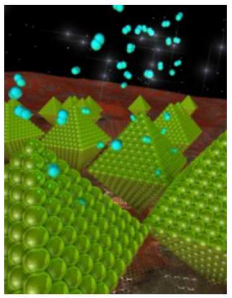
# Accomplishments: HyMARC Phase 1 by the numbers

- **> 50 journal articles published**
  - Including articles in *Energy Env. Sci.*, *Chem. Rev.*, *Adv. Mater. Interfaces*, *Nat. Commun.*, *Adv. Funct. Mater.*, *Nano Lett.*, *Chem. Mater.*
  - 4 articles on journal covers
  - 1 HOT article (in *En. Environ. Sci.*)
- **4 patents (3 issued, 1 applied)**
- **Numerous invited talks** (major international meetings, academic, gov't institutions)
- **6 Symposia and workshops organized** at major conferences
- **> 20 postdocs supported**
- **Global connectivity** through extensive network of collaborations









# Approach/HyMARC-2 Energy Materials Network: enhanced, highly coordinated capabilities to accelerate materials discovery

**Seedling Projects**

- **Applied material development**
  - Novel material concepts
  - High-risk, high-reward
- **Concept feasibility demonstration**
- **Advanced development of viable concepts**


- **Foundational R&D**
- **Computational models**
- **Synthetic protocols**
- **Advanced characterization tools**
- **Validation of material performance**
- **Guidance to FOA projects**
- **Database development**

# Approach Phase 2: Build on Phase 1 discoveries using multi-lab Focus Area teams with interdisciplinary expertise

**Tom Gennett (NREL)**
**Co-Director**

**Mark Allendorf (SNL)**
**Co-Director**

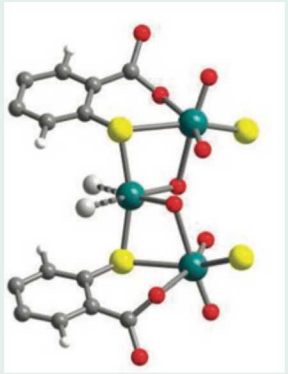
| Task 1 | Task 2 | Task 3 | Task 4 | Task 5 | Task 6 |
|---|---|---|---|---|---|
| **Sorbents** | **Hydrides** | **Carriers** | **Adv. Char.** | **Seedling Support** | **Data Hub** |
| Gennett | Allendorf | Autrey | Parrilla (NREL validation) Prendergast (ALS, SLAC, MF) Bowden (PNNL NMR) Brown (NIST Neutron) Toney (SLAC, X-ray) | Allendorf Gennett | Munch (NREL) |
| **Focus Areas** | **Focus Areas** | **Focus Areas** | **Focus Areas** | | |

**Task leads:**
Coordinate work
Milestone accounting
Reporting

**Focus Areas (new concept):**
Multi—lab Research clusters
Defined topic
Dynamic, agile
Duration: as little as 1 year
Applied topics: Go/No-Go
Foundational topics: milestones

# Sorbents Phase 1 Accomplishments: moved the bar toward materials that meet DOE targets

**Multiple molecular $H_2$ adsorption:** First sorbent material with validated existence of two $H_2$ molecules adsorbed per metal center

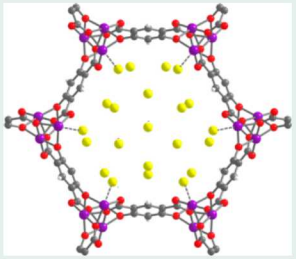


→ *Doubles the volumetric capacity*

- *Chem. Commun.*, 2009, 2296
- see Slide 27 and ST130 for more information

**Highest validated volumetric capacity at room temperature to date:**

Ni(m-dodbc): 11.0 g/L at 25 ˚C and 23.0 g/L for 5→100 bar pressure swing, −75 → 25 ˚C temperature swing



→ *Demonstrates high capacity under realistic operating conditions*

- *Chem. Mater.* 2018, **30**, 8179

**$H_2$ binding energy in a MOF:** approaching 15 kJ $mole^{-1}$ HSEngCOE target

Ni(m-dodbc) Qst = 13.7 kJ $mol^{-1}$

→ *Moving significantly closer to ambient-temperature storage*

- *Chem. Mater.* 2018, **30**, 8179

**New methodologies for validation**

*Improved accuracy of sorbent gas uptake measurements*

- P.A. Parilla et al. *Appl. Phys. A* **122** (2016), 201
- K. E. Hurst et al. *Appl. Phys. A* **122:42** (2016) **DOI:** 10.1007/s00339-015-9537-x

# Approach Sorbents Phase 2: building on Phase 1 discoveries

**Key issues being addressed in Phase 2**

- Need thermodynamics under practical conditions
- Crystallite size/shape/packing must be enhanced to improve capacity
- Can we tailor isotherms to increase capacity (5 – 100 bar swing)?
- Can volumetric density of strong-binding sites be increased?

**Strategies based on Phase 1 results**

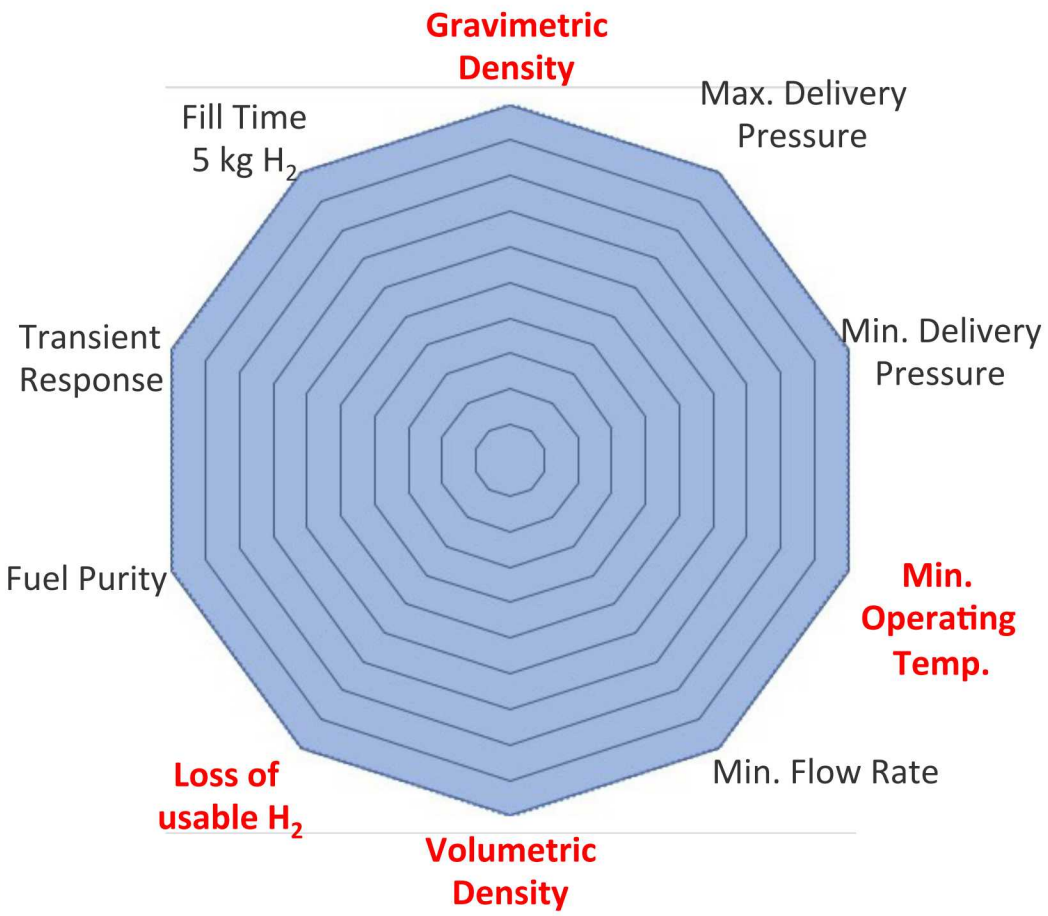
Volumetric/gravimetric capacity

- Bind multiple $H_2$ to open metal sites
- Sol-gel, compaction, particle shape control methods
- Design structurally dynamic MOFs

Operating temperature

- Functionalize MOFs to add strong-binding sites
- MOFs with metals in low oxidation states (e.g. V(II) )

**DOE Targets** we are focusing on are shown in **red**



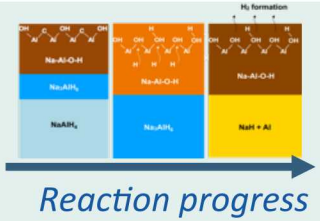
# Approach Sorbents Phase 2 Focus Areas: the path forward

| Focus Area | Focus Area project | DOE Targets: Grav. Capacity | DOE Targets: Vol. Capacity | DOE Targets: Min. Deliv. T | DOE Targets: Min. Deliv. P | Team |
|---|---|---|---|---|---|---|
| **Thermodynamics** | Enthalpy/Entropy under practical conditions | | | X | X | LBNL, NREL, PNNL |
| **Adsorption energy to strong-binding sites** | Electronic structure computations | X | X | | | LBNL |
| | Synthesis: π-basic metals | X | X | | | LBNL |
| | Synthesis: B/N Doping | X | X | | | NREL, PNNL |
| | Synthesis: highly polar open frameworks | X | X | | | NREL, LBNL |
| **Sorbent packing** | MOF monolith synthesis | | X | | | LBNL, SNL |
| | Packing protocol | | X | | | NREL |
| **Dynamic sorbents** | Flexible MOFs | | X | | X | LBNL, NREL |
| | Thermal/photo-responsive sorbent matrices | | X | | X | NREL, LBNL |
| | Multiple $H_2$ binding | | | X | X | LBNL, NREL, NIST |
| | Nanoscale defects in sorbents | X | X | | | SNL, NREL, LBNL |

# Hydrides Phase 1 Accomplishments: moved the bar toward materials that meet DOE targets

**Min. operating T, P:** Oxygenated surface species role in dehydrogenation

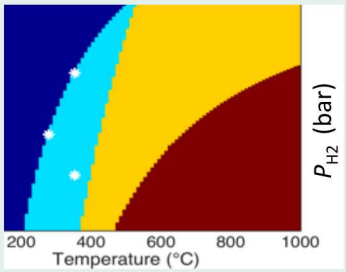
→ *Paradigm shift in understanding of hydride surface chemistry*




**Min. operating T, P:** comprehensive phase diagram for $Mg(BH_4)_2$

$\Delta H°$ = 48 kJ $mol^{-1}$ (HSECoE target is 27 kJ $mol^{-1}$) →

→ bulk $Mg(BH_4)_2$ cannot meet DOE target




**Min. flow rate:** $Mg(BH_4)_2$@Carbon $H_2$ desorption T reduced by >100 °C

→ *Borohydride activation energy reduction by nanoscaling*

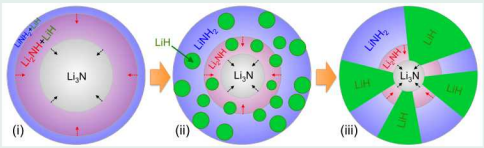
**Gravimetric capacity:** $Mg(BH_4)_2$@rGO >10 wt%

→ *Record capacity for nanoencapsulated complex metal hydride*

**Min. operating T:** $Li_3N$@(6nm-C) $H_2$ delivery T reduced by >180 °C

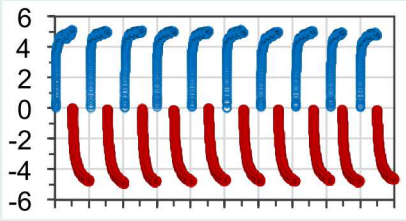
Bulk (430 °C) → Nano (250 °C)

→ *Reaction path modification through nanointerface engineering*




**Improved cycle life:** $Li_3N$@(6nm-C) reversible >5 wt% $H_2$/250 °C/50 cycles

→ *Demonstrates durability of nanoscaled materials*




See also Slide 29 and ST132 for related information

# Approach Hydrides Phase 2: building on Phase 1 discoveries

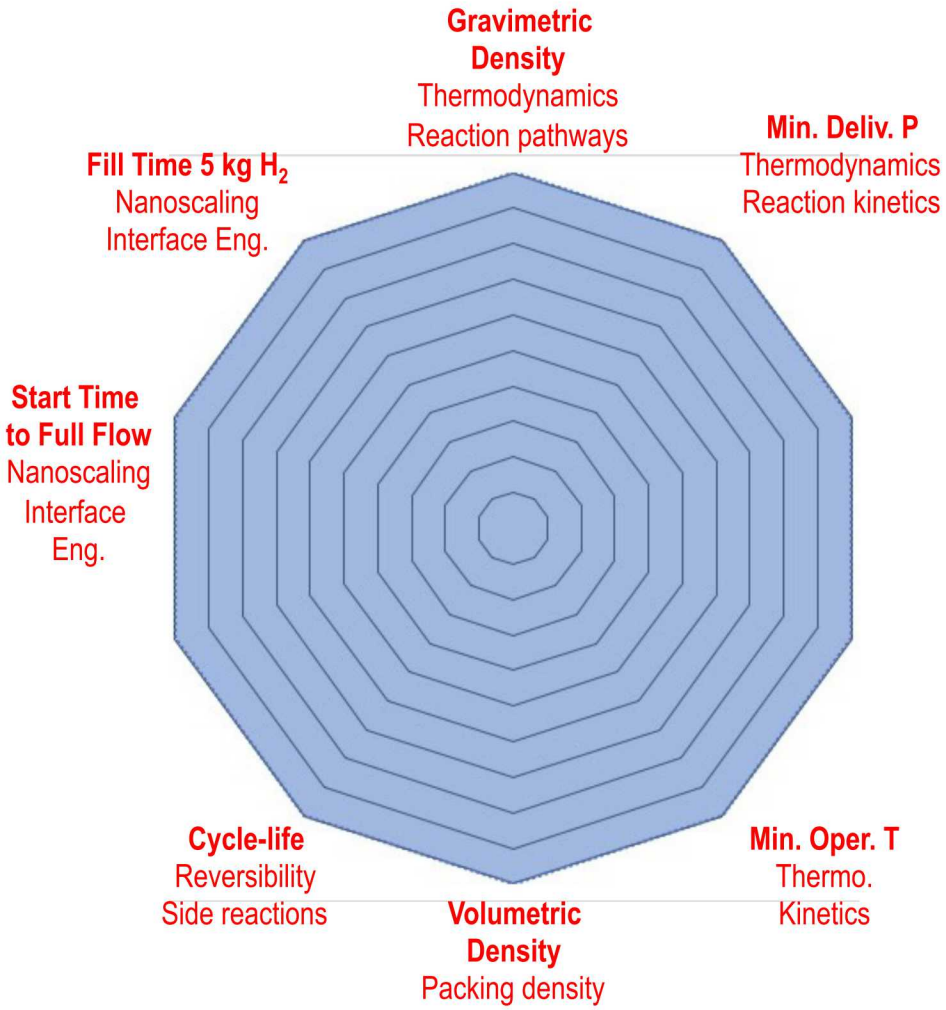
**Science questions (selected)**

- Are there undiscovered phases with favorable thermodynamics ≤27 kJ/mol $H_2$?
- Can nano-scale strain destabilize certain hydrides
- What are rate-limiting steps?

**Strategies derived from Phase 1:**

- Focus on relevant composition spaces
  - Borohydrides
  - Li-N-H
  - Ternaries (e.g. Li-B-Mg-H)
- Determine accurate phase diagrams
- Build on Phase 1 nanoscaling results
- Multiscale modeling to identify rate-limiting processes
- Target additives for specific bond activation
- Probe buried interfaces and surfaces using Phase 1 diagnostic tools
- Develop machine learning as new hydride material discovery capability

**DOE Targets** are interrelated but we are focusing on a key subset (shown in **bold**)



# Approach Hydrides Phase 2 Focus Areas: the path forward

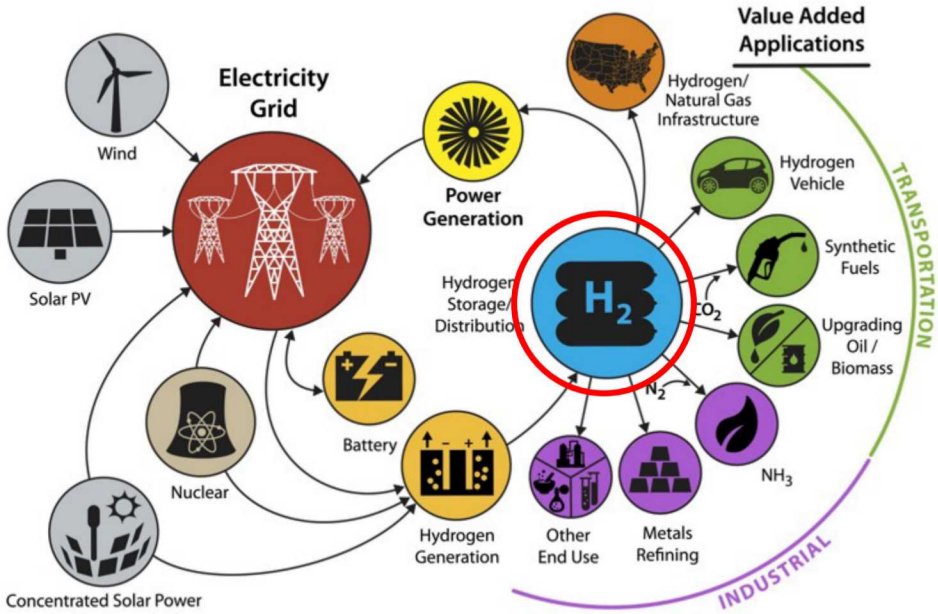
| Focus Area | Focus Area project | DOE Targets: Grav. Capacity | Vol. Capacity | Fill time | Time to full flow | Min. Deliv. T | Min. Deliv. P | Cycle life | Team (lead org. is underlined) |
|---|---|---|---|---|---|---|---|---|---|
| ~~Thermo.~~ | Phase diagrams: ternaries | X | X | | | X | X | | LLNL, SNL, PNNL |
| | Phase diagrams: eutectics | X | X | | | X | X | | SNL, LLNL, PNNL, NRE |
| | Large-scale atomistic models | X | X | X | X | | | | SNL, LLNL |
| Surfaces Interfaces | Interface Model Development | | | X | X | | | X | LLNL, PNNL, SNL |
| | Non-ideal surfaces; phase nucleation | | | X | X | | | X | SNL, LBNL, NREL, LLNL |
| ~~Additives~~ | Modulation of B-H bond strength | | | X | X | X | | | LBNL, NREL, PNNL |
| | Additives for B-B rehydrogenation | | | X | X | X | | | SNL, LLNL, LBNL, PNNL |
| | Modeling B-B/B-H catalytic activation | | | X | X | X | | | LLNL, SNL, LBNL, PNNL |
| Nano strategies | Nano-MH under mechanical stress | | | X | X | | | | LLNL, NREL, LBNL, PNNL |
| | Non-innocent hosts see slide 30 and ST182 | | | X | X | | | | SNL, LLNL, LBNL |
| | $MgB_2$ nanosheets | | | X | X | X | X | | LBNL, LLNL, SNL |
| | Microstructural impacts | | | X | X | | | X | LLNL, LBNL, SNL |
| | Machine learning | X | X | | | | | | SNL, LLNL |

# Relevance: Hydrogen carriers: a new effort initiated in Phase 2

- Bulk storage and transport are of central importance to the H2@Scale concept
- Highly varied storage needs:
  - Daily to seasonal in duration
  - Transport distances > 100s of km

<u>Goal</u>: new concepts and materials that provide advantages over conventional compressed and liquefied hydrogen for bulk storage and transport

H2@Scale concept



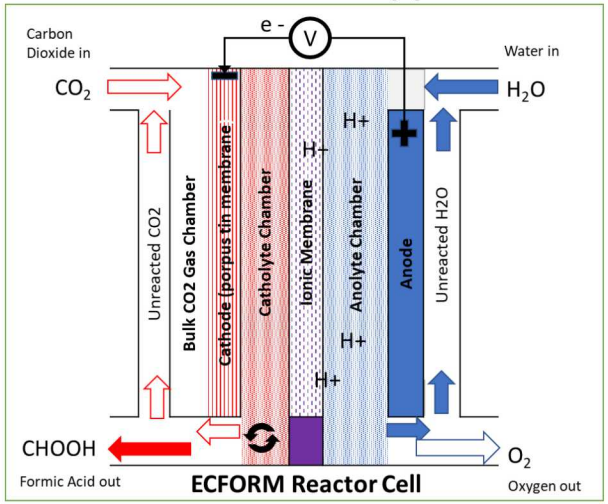

To learn more, see the HyMARC Hydrogen Carriers Webinar:
https://www.energy.gov/eere/fuelcells/downloads/hydrogen-carriers-bulk-storage-and-transport-hydrogen-webinar

# Approach Hydrogen Carriers: Leverage capability and expertise in HyMARC consortium to accelerate progress

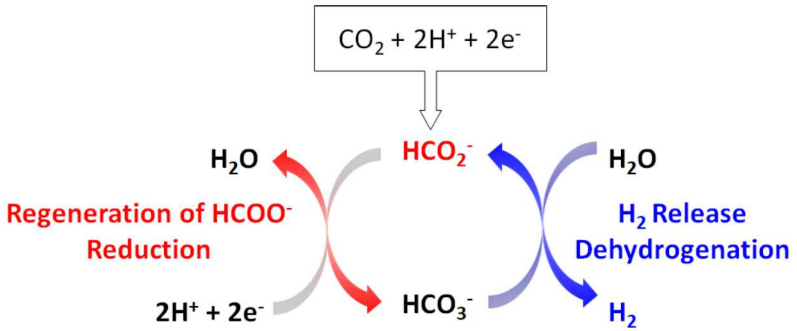
- **Metrics & targets:** Define the important properties of storage materials beyond onboard vehicular
- **Techno-economic analysis:** Determine advantages and limitations of materials and approaches to hydrogen carriers for transport and long-term storage
- **Novel material concepts: identify, characterize, and validate**
  - Approaches to release or 'adsorb' hydrogen onto carriers
  - No discrete step of making $H_2$(gas)
  - Approaches to prevent phase changes
- **Catalysts: optimize the balance of properties:**
  - Stability (TON)
  - Rates (TOF)
  - Cost
  - Selectivity
  - heterolytic vs. homolytic $H_2$ activation

**Examples of carrier strategies under consideration**

**Electrochemical approaches**




**Formate/bicarbonate cycle**

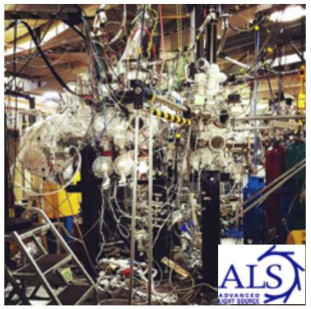


# Approach Carriers Phase 2: nascent Focus Area projects

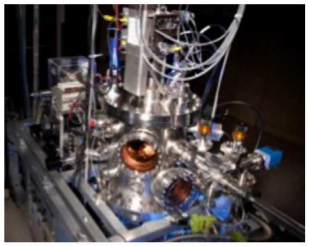
| | Focus Area project | Team |
|---|---|---|
| | Hydrogen carrier production without direct $H_2$ generation | PNNL |
| Liquid organic carriers | Dehydrogenative coupling in LOCs | PNNL |
| | Aqueous organic carriers | PNNL |
| | Formate/bicarbonate cycle See slide 31 | PNNL |
| | Liquid hydrogen carrier capacity determination | NREL |
| | Characterization methods and development | PNNL, NREL |
| | Eutectic systems | SNL, NREL, PNNL |
| Adsorbents as carriers | Analysis of sorbents as hydrogen carriers | LBNL |
| | Porous liquids | NREL, LBNL |
| Novel material concepts | Bioinspired materials | NREL |
| | Plasmon interactions for "On-Demand" $H_2$ release | NREL, LBNL |
| | Heterolytic cleavage and $H_2$ activation | PNNL, NREL |
| | Catalyst stability | LLNL |

# Phase 1 Accomplishment: comprehensive suite of characterization tools (in-situ, operando, all relevant length scales)

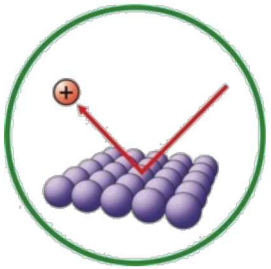
**Atomic/molecular (0 – 1 nm)**



AP-XPS
ALS/BL 11.0.2



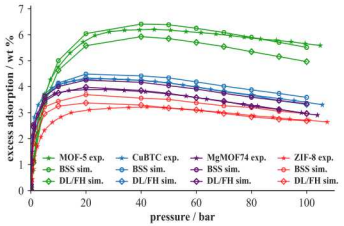
Lab-based AP-XPS

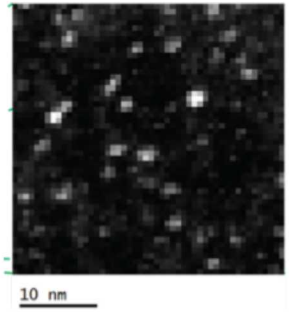


Low Energy Ion Scattering

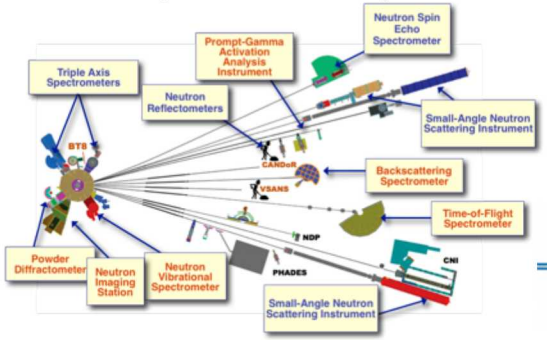
**Molecular/micro (0.5 – 2 nm)**

Microporosimetry/BET

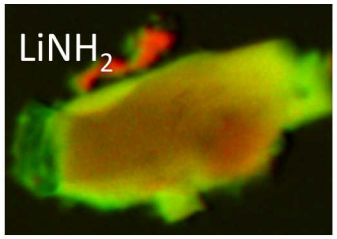


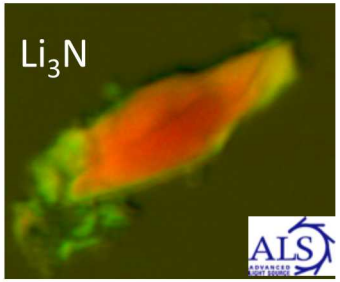




AC-TEM/STEM res. 63 pm




**Mesoscale (2 - 100 nm)** **Grains (≤ 10 μm)**




STXM (30 nm res.)

Neutrons:
- Spectroscopy
- Scattering
- Diffraction

NIST Center for Neutron Research

**Macroscale/Bulk**

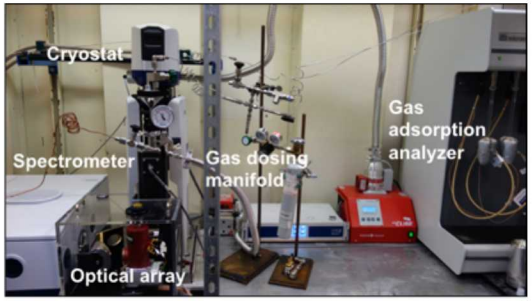
Ultrahigh Pressure Reactor (1000 bar)

H-D exchange

$10^{-10}$ $10^{-8}$ $10^{-6}$ $10^{-4}$ $10^{-2}$
Length (m)

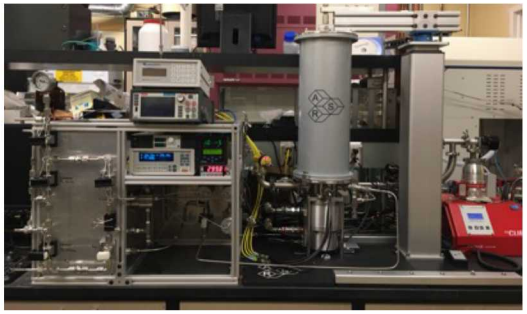
# Phase 1 Accomplishment: extended characterization capabilities

**DRIFTS**



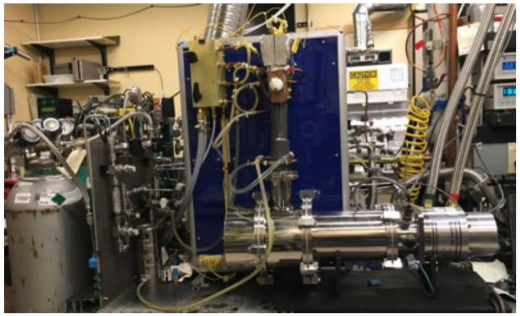

- Diffuse reflectance system coupled to cryostat and gas adsorption analyzer
- Can collect data at 15-373 K and 0-100 bar (controlled dosing up to 1.2 bar)

**Thermal Conductivity**



- $H_2$, He, $CH_4$, $CO_2$ from vacuum to 100 bar
- Temperature Range: 40 K to 375 K
- Sample types include solids & compressed pucks & powder

**Variable Temperature PCT**



- Modified PCT Pro system with capabilities of hydrogen pressures up to 200 bar, and a controlled temperature range from 40 – 350 K. (other gases possible including $CH_4$)
- New methodologies for increased measurement accuracy

P.A. Parilla et al. *Appl. Phys. A* **122** (2016), 201

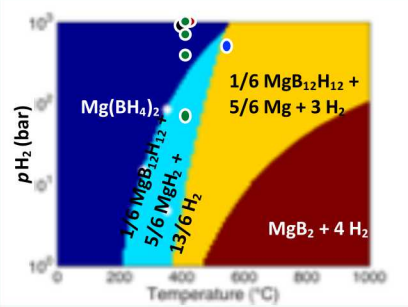
# Approach Characterization Phase 2 Focus Areas: develop and enhance our Phase 1 advanced characterization capabilities

| | Focus Area Topic | Team |
|---|---|---|
| | High-Temperature Validated PCT System | NREL, SNL |
| | PCT Calorimetry See slide 28 and ST131 | NREL, PNNL |
| NMR | Advanced NMR: NMR-FTIR-PCT instrument | LBNL (Long) |
| | High-Temperature/Low-pressure NMR capability | PNNL (Bowden) |
| Advanced in-situ/ex-situ tools | Advanced in-situ, ex-situ Diffraction | SLAC, NIST |
| | Small-Angle X-ray Scattering | SLAC, NREL |
| | XAS/EXAFS | LBNL-ALS, SLAC |
| | Soft X-ray microscopies | LBNL-ALS |
| | Ambient-Pressure XPS | SNL, LBNL-ALS |
| | ATR DRIFTS for liquid carriers | LBNL |
| Neutron techniques | High-P/variable-T for Neutron Scattering Measurements | NIST |
| | Quasi-Elastic Neutron Scattering (QENS) | NIST |
| | VISION (highest resolution broadband INS | ORNL |

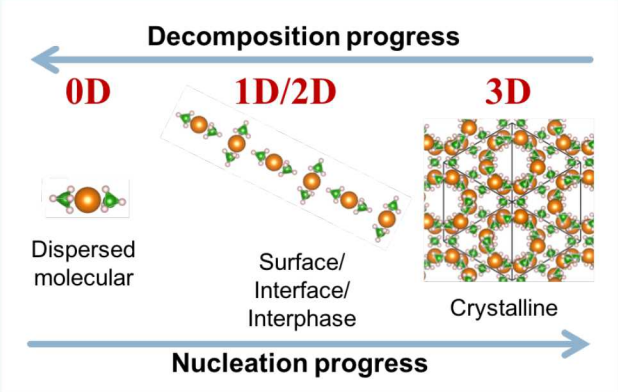
# Phase 1 Accomplishment: Multiscale modeling from understanding to design

See ST129 for more information

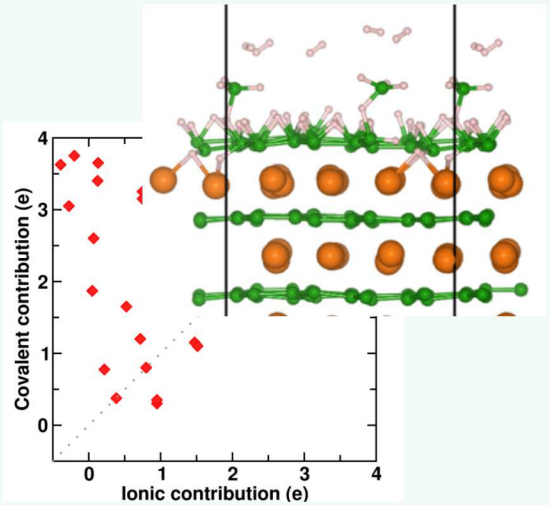
## Predicting phase diagrams



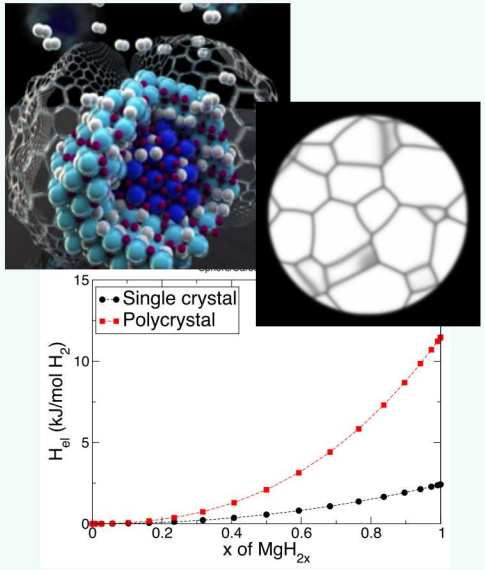

## Simulating nucleation kinetics



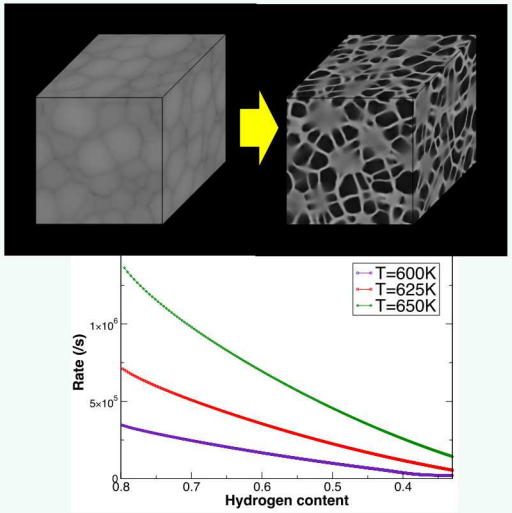

## Understanding catalyst functionality



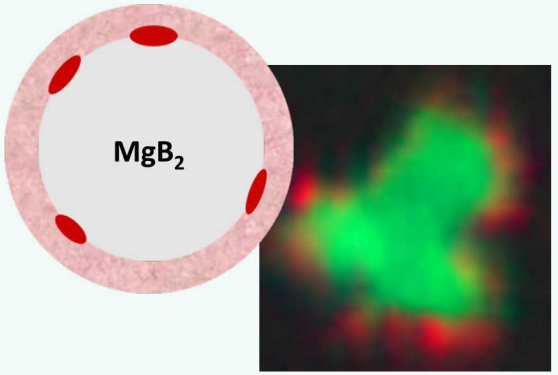

## Assessing tunability via nanoconfinement




## Direct modeling of isotherm uptake




## Interpreting experiments



# Collaboration & Coordination: HyMARC currently collaborates with Phase 2 Seedling

**Seedlings: the HyMARC team assists individual projects with:**

- **A designate HyMARC point-of-contact**
- **Technical expertise concerning specific scientific problems**
- **Access to HyMARC capabilities**
- ***Development of Magnesium Boride Etherates as Hydrogen Storage Materials*** (U. Hawaii)
  - Instability in $MgB_2$ B sheets explained (LLNL modeling investigation)
  - High-P hydrogenation, XRD, and FTIR performed for 43 $MgB_2$(etherate) samples
- ***Electrolyte Assisted Hydrogen Storage Reactions*** (Liox Power)
  - 1) High-P experiments and sample characterization; 2) Go/No-go tests
- ***ALD Synthesis of Novel Nanostructured Metal Borohydrides*** (NREL)
  - Nano-$Mg(BH_4)_2$ nanoparticle samples sent to NREL for ALD coating
- ***Optimized Hydrogen Adsorbents via Machine Learning & Crystal Engineering*** (U. MI)
  - Discussions on crystal engineering of OMS in MOFs

**Selected international collaborations**

- **Hydrides**
  - **KAIST Korea (Prof. Eun Seon Cho): strain-induced effects**
  - **Aarhus Univ. Denmark (Prof. Torbin Jensen): borohydrides**
- **Sorbents**
  - **Univ. Cambridge (Prof. David Fairen-Jamez): MOF consolidation methods**
- **Carriers**
  - **AIST (Prof. Qiang), *in–situ* solution NMR**

# Proposed future work (Any proposed future work is subject to change based on funding levels.)

**Project level**

- Assess effectiveness of management structure and communications
- Evaluate progress of "applied" Focus Areas
- Renew Approved Program at LBNL/ALS for dedicated access to beam lines
- Establish access to VISION high-resolution instrument at ORNL/SNS

**Data hub**

- Begin uploading data to Data Hub, including DOE Hydrogen Storage Database

**Sorbents**

- Establish new models for determining isosteric heats and entropy from PCT data
- New methods for powder compaction, including gel formation and physical methods

**Hydrides**

- Activation of B-B and B-H bonds: *Demonstrate computational approach to enable screening of additives to activate B-B bonds in $MgB_2$.* **(in progress, on track)**
- Reversible capacity: Demonstrate >6% reversible capacity for at least one Li-N-H or Mg-N-H phase, based on predicted composition from phase diagram, with reasonable kinetics at a temperature of ≤ 300 ˚C

**Carriers**

- Carrier material approaches: Determine state-of-the-art

**Advanced characterization**

- Validate the new operational fluidized bed heated PCT System for temperatures up to 375 ˚C and pressures of 150 bar

# Summary

**HyMARC Phase 2 National Laboratory team activities continues:**

- **Foundational research to accelerate materials discovery**
- **Development of advanced characterization tools**
- **Computational modeling across all relevant length scales**
- **Innovative material synthesis**
- **Innovative materials development**
- **Collaboration and assistance to Seedling projects**

**A new *Hydrogen Carriers* initiative was started (Tom Autrey, PNNL, lead)**

**A new Data Hub task was initiated (Kristin Munch, NREL, lead)**

**Organization/management structure revised:**

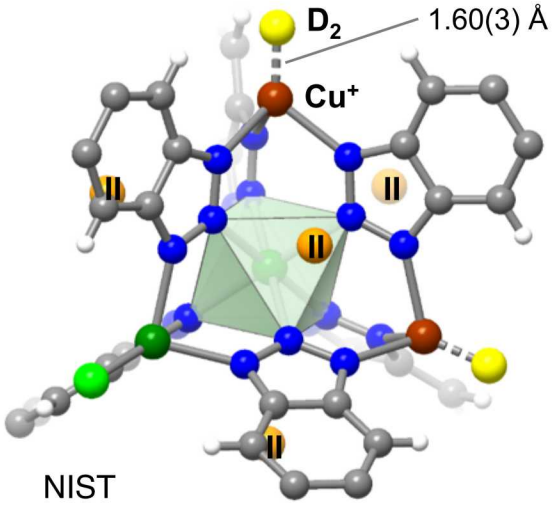
- **"Focus Area" projects developed to enable more agile, intensive research on specific areas**
- **Primary topic areas (e.g., Sorbents, Hydrides, etc.) have lead PI to ensure activities and progress remain on track**

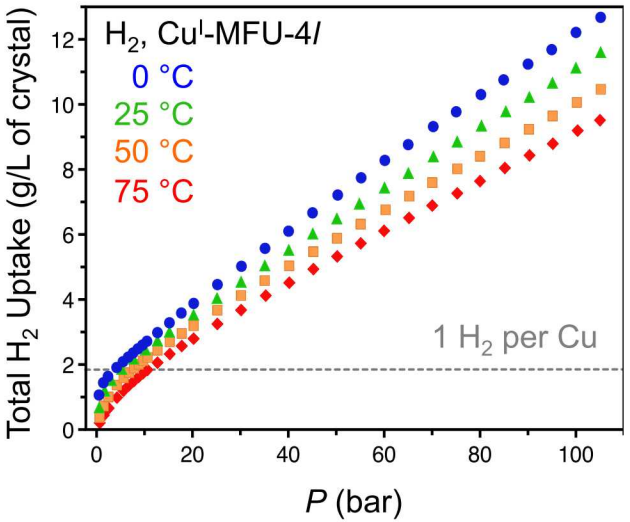
**We are grateful for the financial support of EERE/FCTO and for technical and programmatic guidance from Dr. Ned Stetson, Jesse Adams, and Zeric Hulvey**

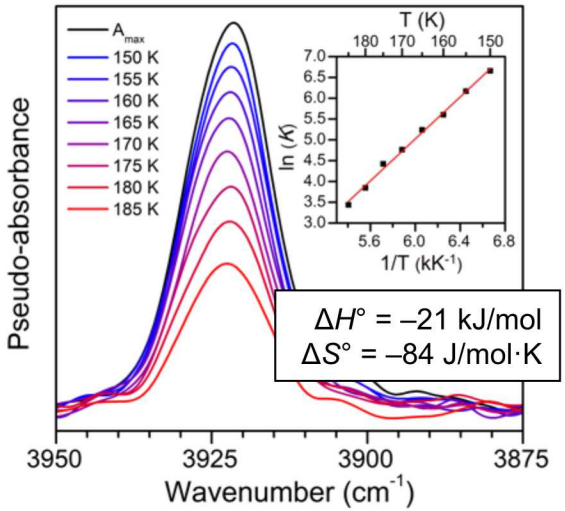

***Enabling twice the energy density for onboard $H_2$ storage***

# Technical Back-Up Slides

# Increasing $H_2$ Binding Energies - LBNL



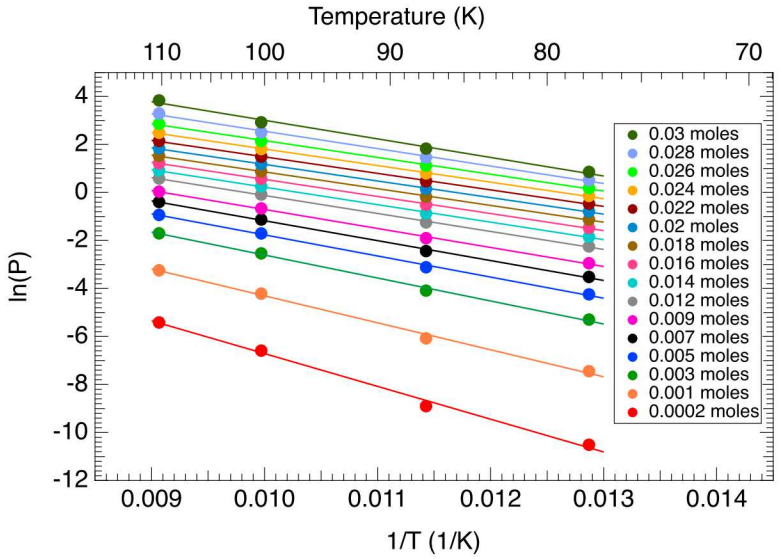



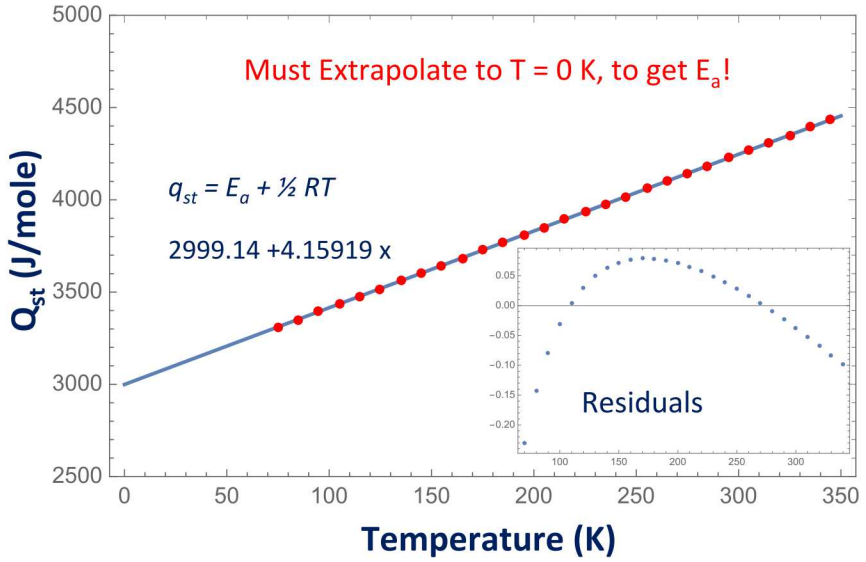

- ***In situ* powder neutron diffraction:** Extremely short Cu–$D_2$ distance observed in Cu$^I$-MFU-4*l* by neutron powder diffraction. Corroborates strong binding enthalpy and large red-shift of $\upsilon$(H–H) observed from DRIFTS.
- **High-P adsorption:** Open $Cu^+$ sites saturate at relatively low pressures. Volumetric usable capacity for Cu$^I$-MFU-4*l* surpasses $Ni_2$(*m*-dobdc) at 75 °C.
- **DRIFTS in $V_2Cl_{2.8}$(btdd):** VTIR confirms high enthalpy of adsorption. Enthalpy–entropy relation distinct from $M_2$(dobdc) family.

# Thermodynamics and Isosteric Heats (NREL)

- Milestone to determine $Q_{st}$ at various T and to validate Cryo-PCT system completed in 2018
- Effort raised several issues about $Q_{st}$ determination & motivated further investigation
- Modeling indicates that several types of bias can be introduced into this determination
- Fundamental assumptions are not valid in the supercritical state

Range from 9-6kj/mole

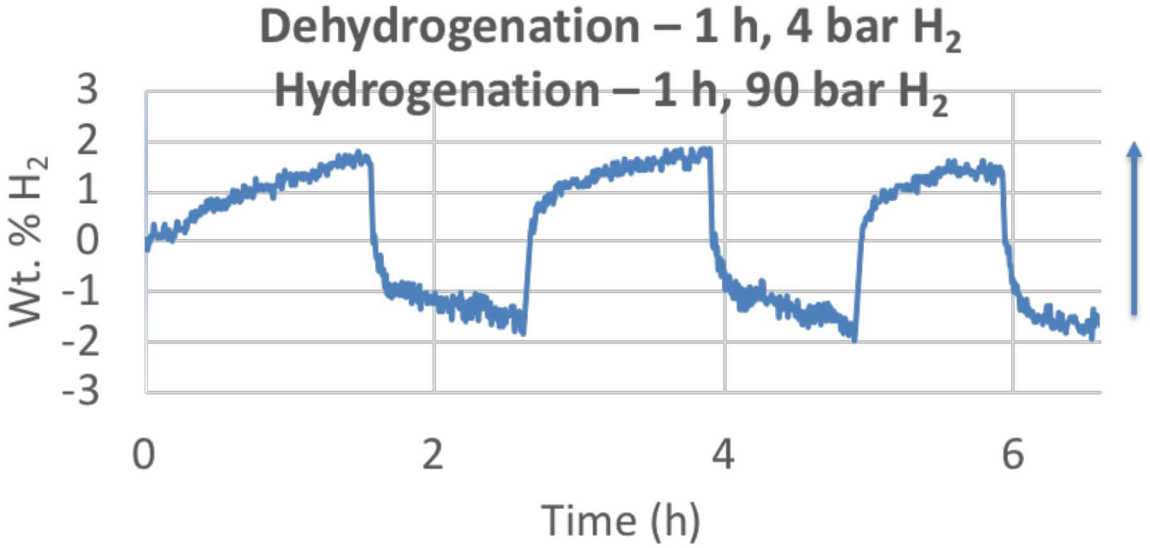


# Highlight - Collaborative effort to understand the limitations to cycling $Mg(BH_4)_2 \Leftrightarrow MgB_{10}H_{10}$

Pacific Northwest NATIONAL LABORATORY

**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 $H_2$?**

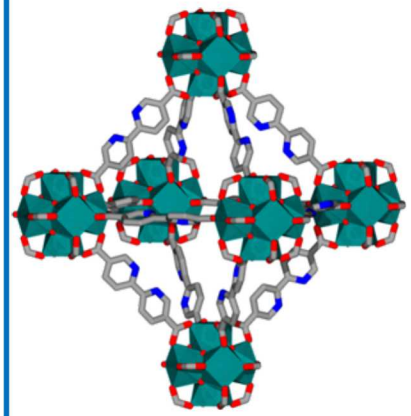



- PCT cycling (Hawaii)
- TPD/MS and DSC (NREL)
- Synchrotron XR (Norway)
- NVS (NIST)
- In-situ NMR, XRD, IR, RAMAN, calc ΔG (PNNL)
- Solvent free (Geneva)

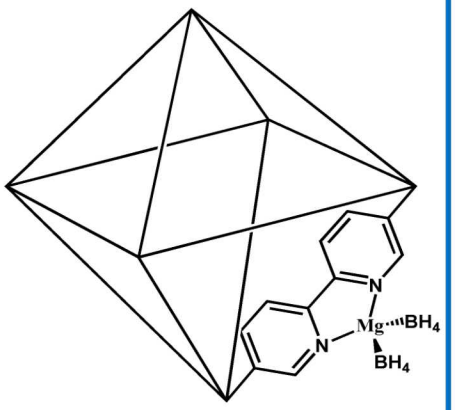
- Thermodynamics favor regen of $Mg(BH_4)_2$ from $MgB_{10}H_{10}$ (ΔH ca. 38 kJ/mol, ΔS ca. 95 J/K/mol, T (1 bar $H_2$) = 135 ˚C
- Additives, e.g., THF lower the mp of $Mg(BH_4)_2$.
- Sub-stoichiometric amounts, e.g., 0.25 THF/Mg results in a mixture of phases.
- Mixture melts between 75 – 100 ˚C to 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.
- Can do fast cycling, but heating too long or cooling to room temperature stops ability to cycle.

# Isolated molecularly dispersed $Mg(BH_4)_2$ species with record low hydrogen release temperature

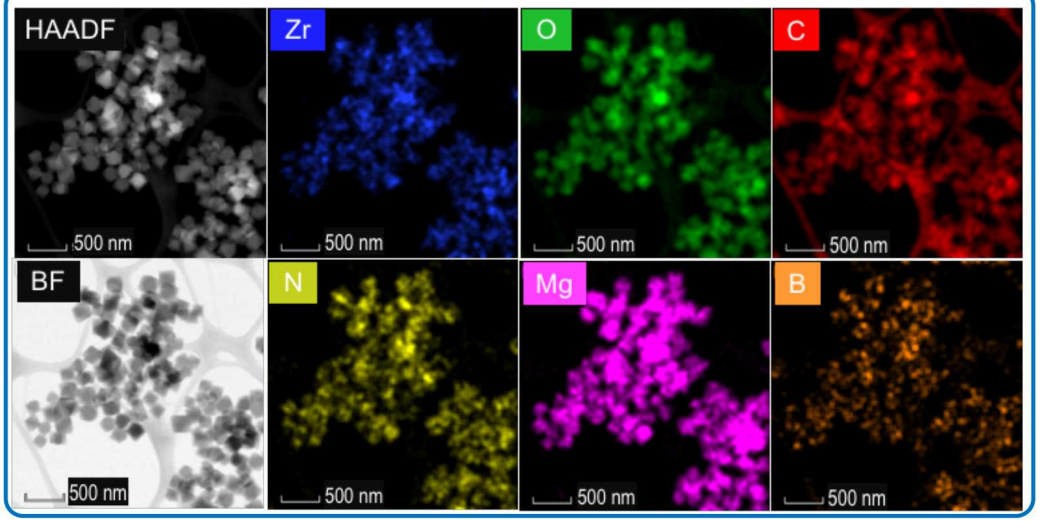
Sandia National Laboratories

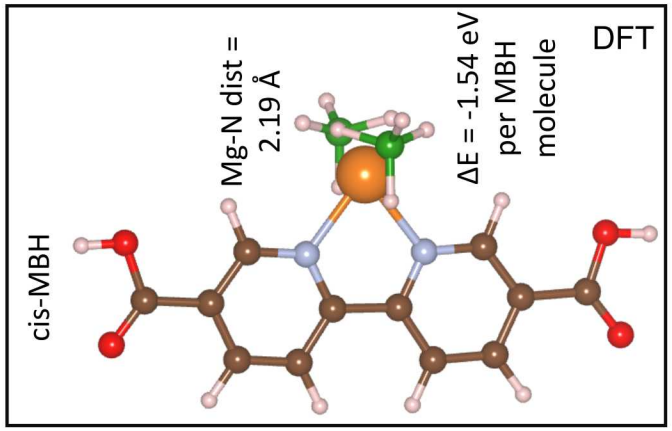


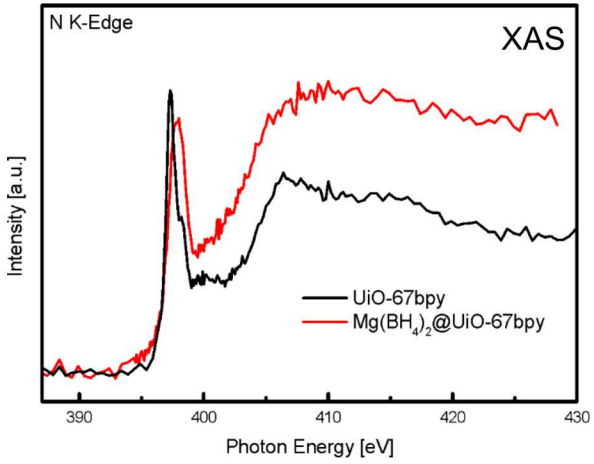
UiO-67-bipy

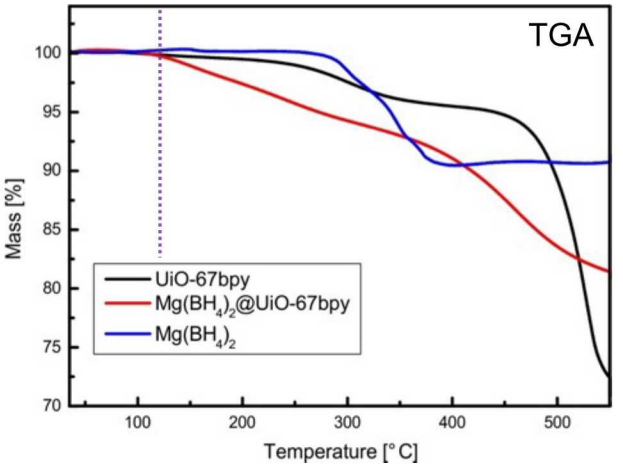



$Mg(BH_4)_2$@UiO-67-bipy




⇒ TEM and XAS data, coupled with DFT calculations, reveal that $Mg(BH_4)_2$@UiO-67-bipy is composed of molecular $Mg(BH_4)_2$ species coordinated to bipyridine groups

⇒ Hydrogen release starts as low as 120 deg. C, >100 deg. C lower than bulk.

# **Carrier concepts:** Chemical compression from formic acid

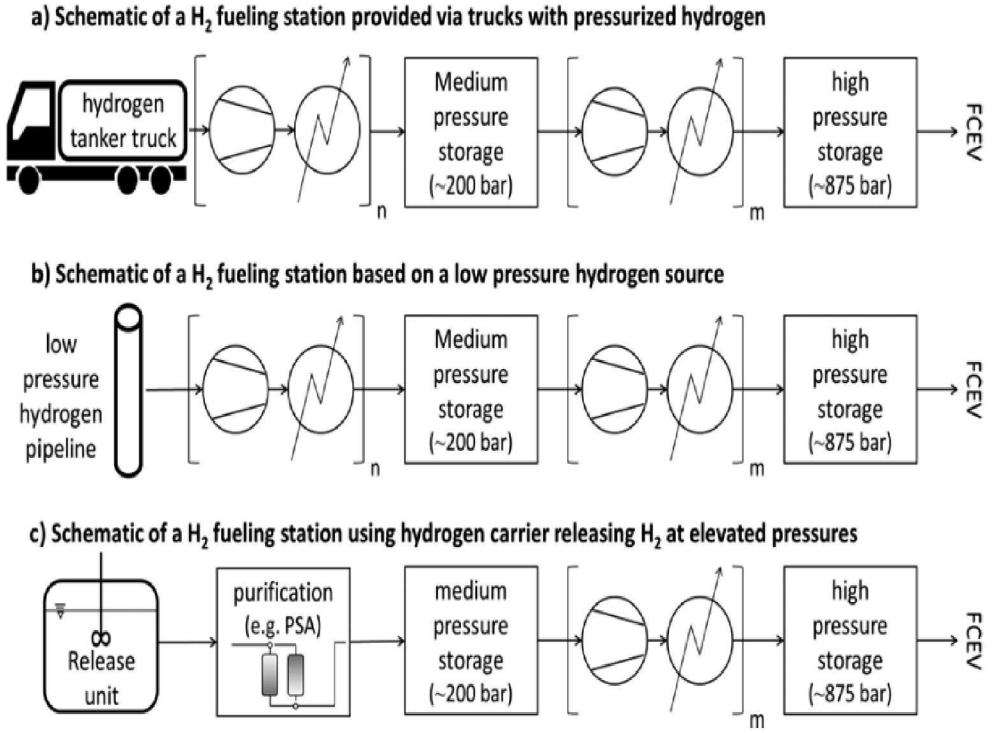
Pacific Northwest NATIONAL LABORATORY

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

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

*Collaboration with Karsten Mueller Hydrogenious*

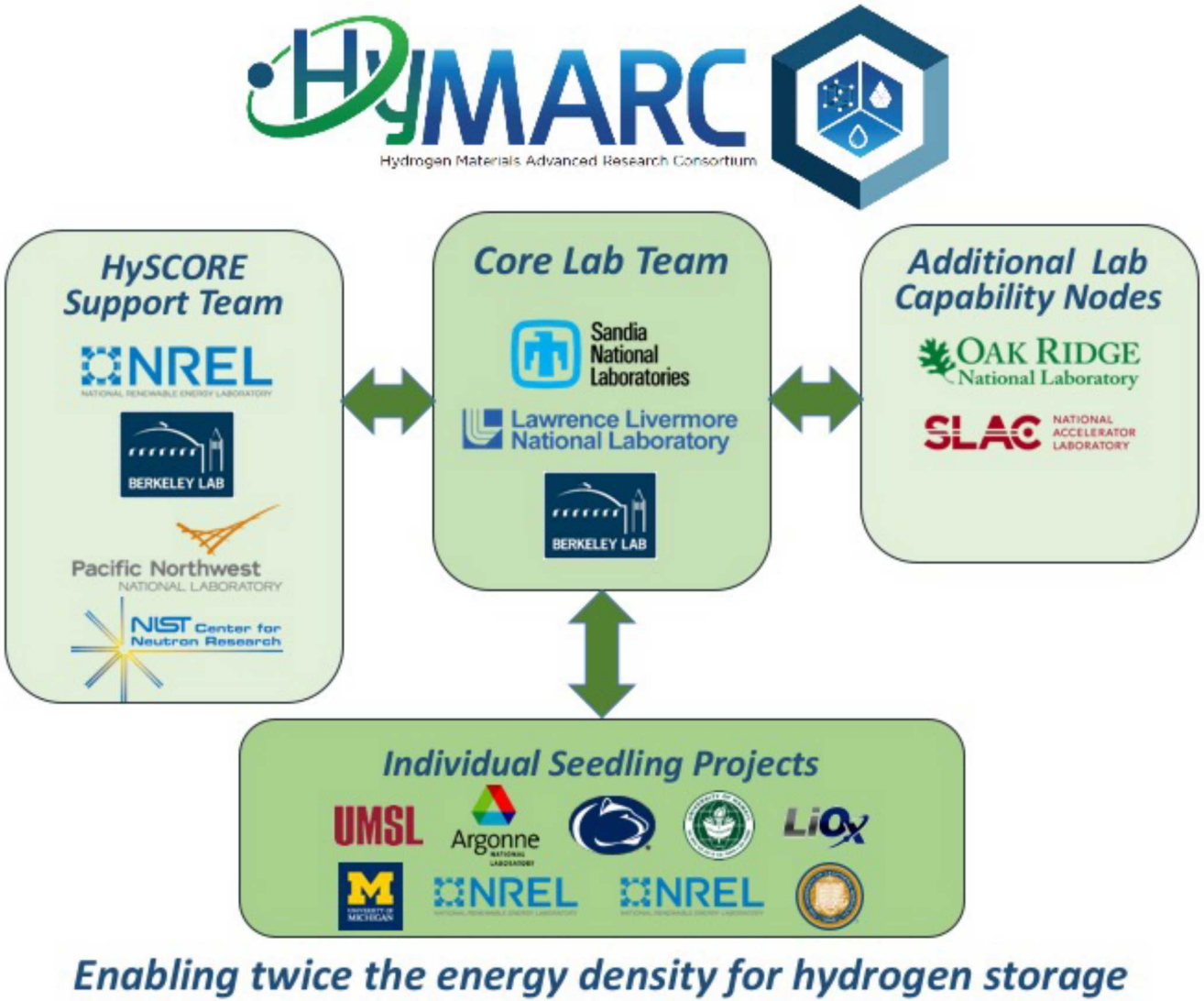
**Schematics of various concepts for hydrogen fueling stations**




*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

# Reviewer-Only Slides

# Approach: Phase 1 (FY16-18) HyMARC structure addressed foundational research objectives and supported Seedling projects



# Approach Phase 2: Management team, Principal Investigators and Lead Researchers guide the research and allocate resources

Mark Allendorf
Co-Director
SNL PI
Hydrides Lead

Tom Gennett
Co-Director
NREL PI
Sorbents Lead

David Prendergast
LBNL Co-PI

Jeff Long
LBNL Co-PI

Brandon Wood
LLNL PI

Tom Autrey
PNNL PI
Carriers Lead

Vitalie Stavila (SNL)
Co-PI, Hydrides

Kristin Munch
Data Hub/Web

Phil Parilla (NREL)
Co-PI, Adv. Charac.

Tae Wook Heo (LLNL)
Co-PI, modeling

**User facility POCs**

Craig Brown

Terry Udovic

Mike Toney

Mark Bowden

Jinghua Guo

David Prendergast

# Reponses to 2018 Reviewer's comments

***The overall recommendation is for a stronger and more streamlined management structure.*** Response: Streamlining the HyMARC management structure without making it highly "top down" is difficult. The Phase 2 Focus Area structure is intended to make communications within specific research areas more efficient and we expect it will create a more horizontal and flexible organization. The Task structure will minimize the number of people involved in administrative activities (e.g. reporting and coordination/communication with DOE). We also designated a PI to lead the Data Hub and web site activities, which removes a significant maintenance activity from the shoulders of the Lab PIs.

***It will be important to add additional chemistry expertise to the team.*** Response: It is difficult to understand this comment, as many of the lead HyMARC research staff are chemists (e.g. Allendorf, Autrey, Head-Gordon, Long, Stavila, and Urban, as well as several postdocs). Moreover, HyMARC is a highly interdisciplinary effort that requires the expertise of materials scientists, physicists, and chemical engineers. Where additional expertise in specific areas is required, we have and will continue to form collaborations with recognized experts.

***Convene a "Hydrogen Summit" with attendees from the consolidated HyMARC core team, DOE Hydrogen and Fuel Cells Program managers.*** Response: This was conducted in April 2018 at NREL and involved research staff and postdocs from all constituent HyMARC laboratories. Its objective was to update the team regarding current status, discuss management structure options, and identify critical research topics for Phase 2. The results of the meeting are reflected in the Phase 2 Annual Operating Plan.

# HyMARC Phase 2 Team Milestones

- **Milestone 1: 12/31/18:** Focus Area 6.1: Data Hub Determine HyMARC Data Needs: *Through meetings between the HyMARC Data Team and technical team members, we will identify data formats, sources and types used across HyMARC. We will develop best practices for data upload and sharing, and usage of defined metadata terms and forms.* **(100% complete)**

- **Milestone 2: 3/31/19**: Focus 3.D.2: Porous liquids as hydrogen carriers: *Porous Liquids: Demonstrate viability of click chemistry or nitrene approach for COF shell functionalization.* **(100% complete)**

- **Milestone 3: 6/30/19:** Focus 2.C: Activation of B-B and B-H bonds: *Demonstrate computational approach to enable screening of additives to activate B-B bonds in $MgB_2$.* **(in progress, on track)**

- **Milestone 4: 9/30/19:** *Demonstrate >6% reversible capacity for at least one Li-N-H or Mg-N-H phase, based on predicted composition from phase diagram, with reasonable kinetics at a temperature of ≤ 300 ˚C. PCT isotherm measurements will be carried out at temperatures ≤ 300 ˚C measuring total hydrogen uptake and release for each cycle. Isotherm plots and total hydrogen uptake and release data will be provided for each cycle. Data indicating at least 6wt% total hydrogen gravimetric capacity with reasonable kinetics at a temperature of ≤ 300 ˚C will constitute meeting the milestone criteria.* **(in progress)**